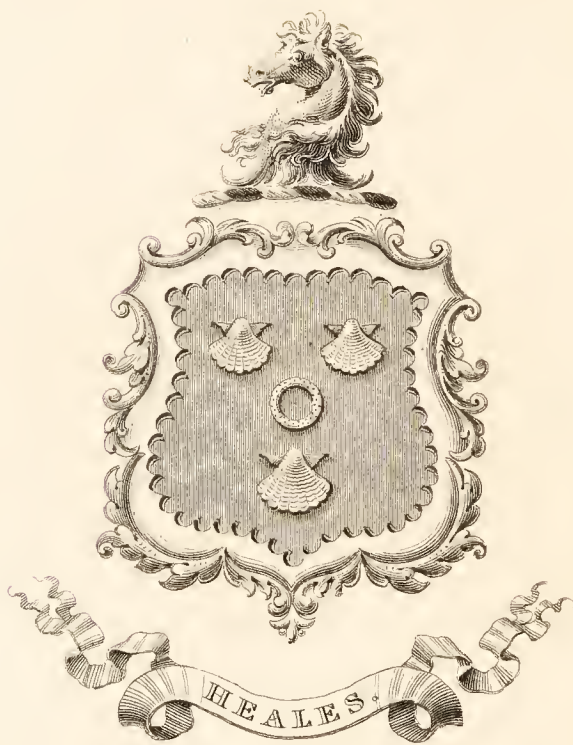


PRIZE FOR  
**CHEMISTRY.**

R. M. ACADEMY.

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MANUAL  
OF  
CHEMISTRY:

BY

WILLIAM THOMAS BRANDE,

*OF HIS MAJESTY'S MINT;*

F. R. S. L. AND E.; PROF. CHEM. R. I., &amp;c. &amp;c. &amp;c.

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PART II.

INCLUDING

THE METALS AND THEIR COMBINATIONS.

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LONDON:  
JOHN W. PARKER, WEST STRAND.

M.DCCCXXXVI.





## CHAPTER VI.

## OF THE METALS, AND THEIR COMBINATIONS.

THE metals constitute a numerous and important class of simple substances. They are forty-two in number.

1. Gold.	15. Manganese.	29. Sodium.
2. Silver.	16. Tungsten.	30. Lithium.
3. Copper.	17. Tellurium.	31. Barium.
4. Iron.	18. Molybdenum.	32. Calcium.
5. Mercury.	19. Uranium.	33. Strontium.
6. Tin.	20. Titanium.	34. Magnesium.
7. Lead.	21. Chromium.	35. Silicium.
8. Zinc.	22. Columbium.	36. Alumium.
9. Bismuth.	23. Palladium.	37. Yttrium.
10. Antimony.	24. Rhodium.	38. Glucium.
11. Arsenic.	25. Iridium.	39. Zirconium.
12. Cobalt.	26. Osmium.	40. Cadmium.
13. Platinum.	27. Cerium.	41. Thorium.
14. Nickel.	28. Potassium.	42. Vanadium.

Of these metals the first seven were known in very remote ages. The ancients designated them by the names of the planets, to which they were supposed to have some mysterious relation; and each was denoted by a particular symbol, representing both the metal and the planet.

Gold	was the Sun,	and was thus represented	☉
Silver	... Moon	... ..	☾
Mercury	... Mercury	... ..	☿
Copper	... Venus	... ..	♀
Iron	... Mars	... ..	♂
Tin	... Jupiter	... ..	♃
Lead	... Saturn	... ..	♄

Zinc was not known to the ancients, though they were probably acquainted with its ores, and with their property of forming brass when fused with copper. (Pliny, lib. xxxiv., cap. 2 and 10.) The word *Zinc* first occurs in the writings of Paracelsus, who died in 1541. Bismuth is mentioned in the *Bermannus* of Agricola, written about 1530. Antimony was first obtained in its pure state by Basil Valentine towards the end of the fifteenth century. The process is described in his *Currus Triumphalis Antimonii*. Arsenic and Cobalt were discovered by Brandt in 1733 (*Acta Upsal.* 1733 and 1742); their ores were known at a much earlier period. Platinum was first recognised as a peculiar body in 1741, by Mr. Charles Wood, Assay-Master in Jamaica (*Phil. Trans.*, vol. xlv.) In 1751, the distinctive characters of Nickel were shown by Cronstedt (*Stockholm Transactions*), and Manganese was obtained by Gahn in 1774 (*Bergman's Opuscula*, vol. ii.) Tungsten was discovered by M.M. Delhuyart, in 1781 (*Mémoires de Toulouse*). Tellurium and Molybdenum by Müller and Hielm, in 1782. Uranium by Klaproth in 1789. Tita-

nium by Mr. Gregor, in 1789. Chromium by Vauquelin, in 1797 (*Ann. de Chim.*, vol. xxv.) In 1802, Mr. Hatchett discovered Columbium (*Phil. Trans.*) Palladium and Rhodium were discovered by Dr. Wollaston; and Iridium and Osmium by Mr. Tennant, all in 1803 (*Phil. Trans.*) Cerium was announced in 1804, by MM. Hisinger and Berzelius (*Gehlen's Journal*, ii.) Potassium and Sodium were discovered in 1807, by Sir H. Davy, whose experiments also led to the discovery of the metallic nature of the ten following bodies. Professor Stromeyer, of Göttingen, discovered Cadmium in 1818. Thorium was discovered by Professor Berzelius in 1829, and Vanadium by Professor Seftström, of Fahlun, in 1830.

Metals are chiefly found in the earth in *veins* which traverse the granitic, schistose, and limestone rocks; and they also occur, although comparatively rarely, in rounded and detached fragments and nodules, disseminated through certain alluvial strata. They seldom occur in an uncombined state, but almost always united to other substances, as in the four following classes:—

i. *Native Metals* are those which occur pure or alloyed, such as platinum, rhodium, iridium, osmium, gold, silver, mercury, copper, antimony, arsenic, and tellurium.

ii. *Metals combined with simple non-metallic substances.* The compounds belonging to this class are the *native metallic oxides*, and *native chlorides*; *iodides* and *bromides* are extremely rare; and there are very few *fluorides*. The *native metallic sulphurets* are a very numerous and important series of ores. The *seleniurets* are very rare. One *native carburet* only is known, that of iron. There are no native hydrurets, phosphurets, nor borurets.

iii. *Metals in combination with acids; Metallic Salts.* Of these the most common are the native *carbonates*, *sulphates*, and *phosphates*: there are a few native *borates*; and a few species belong also to this class in which the oxide is united to a *metallic acid*: such as the *native arseniates*, *chromates*, *tungstates*, *molybdates*, and *vanadiates*.

The metals, as a class, are characterized by *opacity*, and a peculiar *lustre*. Their opacity is such, that even when extended into very thin leaves, they generally transmit no light; silver-leaf, only one one-hundred-thousandth of an inch in thickness, is perfectly opaque. Gold when beaten out into leaves one two-hundred-thousandth of an inch in thickness, transmits green rays of light. Their lustre depends upon their great power of reflecting light, in consequence of their opacity. They are excellent conductors of heat and of electricity. (See pages 143 and 226.)

The polished metals are very imperfect radiators and receivers of heat (page 194); but they are excellent reflectors both of light and heat, and hence their peculiar fitness for the construction of burning mirrors. According to Leslie, the metals, as *reflectors of radiant heat*, may be arranged in the following order, the highest number implying the greatest reflective power:—

Brass	100
Silver	90
Tin	80
Iron	70
Lead	60

Whenever the polish of the metallic surface is impaired, its power of reflecting heat suffers a proportionate diminution, while its power of absorbing, and also of radiating heat, is proportionably increased. (See page 190.)

The greater number of the metals are susceptible of assuming the crystalline form. With many, this may be effected by fusion and slow cooling, and especially by suffering a ladle, or crucible, filled with the melted metal, to concrete externally, and then perforating the solid crust, and pouring out the liquid interior; the cavity so formed will then be lined with crystals: this mode of proceeding answers extremely well with bismuth, which furnishes a singular congeries of cubic crystals (p. 110). When the metals are precipitated by each other, they often crystallize during their deposition, as is seen in the precipitation of silver by mercury, and in that of lead by zinc. A stick of phosphorus immersed in a solution of silver becomes incrustated with beautiful metallic crystals, which, after some time, perfectly encase the phosphorus. Gold is occasionally deposited in a crystalline form, from its nitromuriatic and from its ethereal solutions. Some curious facts, relating to this subject, will be found in a paper by Professor Daniell, "On certain Phenomena resulting from the action of Mercury upon different Metals." (*Royal Instit. Journal*, i. 1.)

There is the greatest difference in the *specific gravity* of the different metals, the heaviest and lightest solids being included in the list. Their specific gravity is also in some instances a little increased by hammering, rolling, and some other mechanical processes by which they are permanently compressed.

The principal metals, arranged according to their specific gravities, stand as follow:—

1. Platinum . . . . .	21.00	13. Nickel . . . . .	8.27
2. Gold . . . . .	19.30	14. Iron . . . . .	7.78
3. Tungsten . . . . .	17.50	15. Molybdenum . . . . .	7.40
4. Mercury . . . . .	13.50	16. Tin . . . . .	7.30
5. Palladium . . . . .	11.50	17. Zinc . . . . .	7.00
6. Lead . . . . .	11.35	18. Manganese . . . . .	6.85
7. Silver . . . . .	10.47	19. Antimony . . . . .	6.70
8. Bismuth . . . . .	9.80	20. Tellurium . . . . .	6.10
9. Uranium . . . . .	9.00	21. Titanium . . . . .	5.3
10. Copper . . . . .	8.89	22. Arsenic . . . . .	5.8
11. Cadmium . . . . .	8.60	23. Sodium . . . . .	0.972
12. Cobalt . . . . .	8.53	24. Potassium . . . . .	0.865

*Malleability.* Among the metals, some are *malleable*, others *brittle*; hence the ancient division into *perfect* and *semi-metals*. Common gold-leaf is not more than  $\frac{1}{200000}$ th of an inch in thickness, and five grains are sufficient to cover a surface of more than 270 square inches. This capacity of being extended by the hammer, belongs to the following metals:—

Gold.	Platinum.	Palladium.
Silver.	Lead.	Potassium.
Copper.	Zinc.	Sodium.
Tin.	Iron.	Frozen Mercury.
Cadmium.	Nickel.	

*Ductility.* The malleable metals are also *ductile*; that is, they admit of being drawn out into wires. A grain of gold may be drawn, it is said,

into 500 feet of wire; and by enveloping it in silver, Dr. Wollaston found that it might be so extended, as that 700 feet weighed only one grain; in thickness, therefore, not exceeding  $\frac{1}{30000}$ th of an inch. The coating of silver was removed by dilute nitric acid. In the same way he has produced platinum wire of similar tenuity. (*Phil. Trans.*, 1813.) The metals are arranged according to ductility as follows:—

Gold.	Copper.	Lead.
Silver.	Zinc.	Nickel.
Platinum.	Tin.	Palladium.
Iron.		

*Tenacity.* Different metallic wires are possessed of different degrees of *tenacity*, by which is meant the power of supporting a weight without breaking. According to the experiments of Guyton Morveau, the following are the weights capable of being sustained by wires 0.787 of a line in diameter. (*Ann. de Chim.*, lxxi.)

	lbs.	dec.
	avoir.	parts.
A wire of iron supports . . . . .	549.250	
„ copper . . . . .	302.278	
„ platinum . . . . .	274.320	
„ silver . . . . .	187.137	
„ gold . . . . .	150.753	
„ zinc . . . . .	109.540	
„ tin . . . . .	34.630	
„ lead . . . . .	27.621	

*Brittleness.* The following metals are so brittle as to admit of being reduced to powder.

Antimony.	Cobalt.	Tungsten.
Arsenic.	Columbium.	Titanium.
Bismuth.	Manganese.	Uranium.
Cerium.	Molybdenum.	
Chromium.	Tellurium.	

*Hardness.* Few of the metals, when pure, are very *hard*, and many so soft as to yield to the nail. In the following table some of the metals are arranged in the order of their hardness:—

Titanium.	Nickel.	Zinc.
Rhodium.	Platinum.	Antimony.
Tungsten.	Copper.	Cobalt.
Palladium.	Silver.	Tin.
Manganese.	Bismuth.	Arsenic.
Iron.	Gold.	Lead.

*Elasticity* and sonorousness belong to the hardest metals only.

Such are the essential physical characters of the metals; they also resemble each other in many of their *chemical properties*, as the following general observations show:—

**ACTION OF HEAT\*.** The metals are all susceptible of fusion by heat,

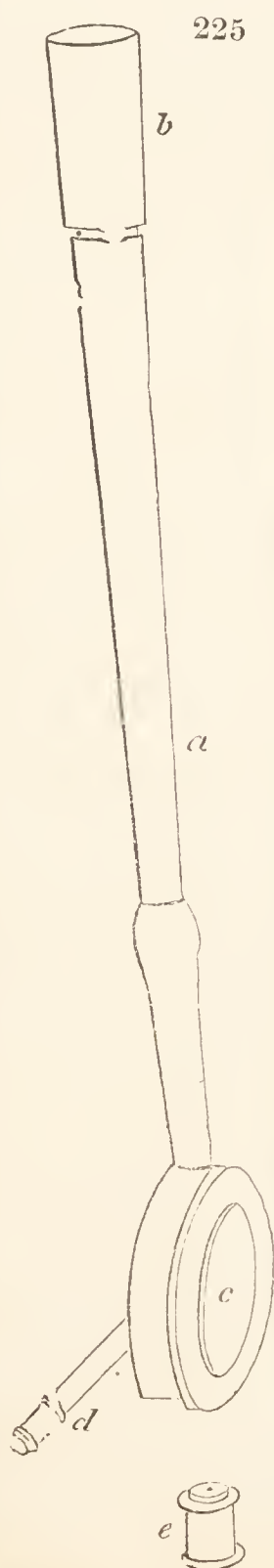
\* In the examination of the effects of heat upon metallic and mineral substances, the *blowpipe* is a most useful and necessary auxiliary to our other operations; it affords a simple and convenient means of heating to a very high degree, and almost instantaneously, any substance sufficiently small to be enveloped in its flame; and the experienced eye is thus frequently enabled to anticipate, with much precision, the nature of the substance submitted to experiment. There are numerous forms of the blowpipe, among which, that represented in

but the temperatures at which they liquefy are extremely various. Mercury is fluid at all common temperatures, and requires to be cooled to  $-39^{\circ}$  before it congeals. Potassium melts at about  $140^{\circ}$ , and sodium at  $200^{\circ}$ ; tin at  $450^{\circ}$ ; lead at  $600$ ; zinc at  $700$ ; and antimony at  $800^{\circ}$ . Silver, gold, and copper, require a bright cherry-red heat; iron, nickel, and cobalt, a white heat; manganese and palladium an intense white heat; molybdenum, uranium, tungsten, and chromium, are only very imperfectly agglutinated at the highest temperatures of our furnaces; and cerium, osmium, iridium, rhodium, platinum, and columbium, require the intense heat produced by an inflamed current of oxygen and hydrogen, or that of Voltaic electricity; and in respect to titanium it is doubtful whether it has ever been fused. Arsenic volatilises before it fuses; but in general, at higher temperatures than that required for their fusion, the metals are volatile, and may be distilled in close vessels. Mercury,

fig. 225 is perhaps the most convenient. It consists of a brass-tube *a*, with an ivory mouth-piece *b*; the other end of the tube terminates in a circular box, from which issues the small tube *d*, moveable in any direction round the centre *c*, by which any degree of obliquity may conveniently be given to the flame; *e* is a brass jet which fits upon the tube *d*.

The following observations respecting the use of the blow-pipe, and its action upon several substances, are extracted from Mr. Children's *Essay on Chemical Analysis*; a work from which the student may derive much valuable information.

A continued stream of air is absolutely essential, to produce which, without fatigue to the lungs, an equable and uninterrupted inspiration must be maintained by inhaling air through the nostrils, whilst that in the mouth is forced



through the tube by the compression of the cheeks. A little practice will make this operation easy, but at first considerable lassitude is generally experienced in the buccinator muscles. Upon this subject, see Faraday's *Manipulation*, sect. iv. After habit has rendered the operation familiar, a current may be kept up for ten or fifteen minutes, without inconvenience. A large wax-candle supplies the best flame, which being urged by the blast, exhibits two distinct figures; the *internal* flame is conical, blue, and well defined, at the apex of which the most violent degree of heat is excited; the *external* is red, vague, and undetermined, and of very inferior temperature to the former.

The substance to be submitted to the action of the blow-pipe, which should not be larger than a small pepper-corn, must be supported either on charcoal, or a slip of platinum or silver foil, or be held in a pair of platinum pincers. In the first case it may be placed in a cavity in the charcoal, and another piece laid over it to prevent its being carried off by the blast. The metallic supports are used when the subject of the experiment is intended to be exposed to the action of heat only, and might be altered by contact with the charcoal. If a very intense heat be required, the foil may be laid on charcoal. Salts and volatile substances are to be heated in glass tubes, closed at one end, and enlarged according to circumstances, so as to form small matrasses.

The exterior flame should first be directed on the substance, and when its action is known, then the interior blue flame. Notice should be taken, whether the matter decrepitates, splits, swells up,

cadmium, arsenic, potassium, sodium, tellurium, and zinc, are volatile at a red heat. Gold and silver are converted into vapour when exposed to the intense heat of the focus of a burning lens; and several of the other metals boil and evaporate under similar circumstances. It is probable that this would happen to all of them, if raised to sufficiently high temperatures.

liquefies, boils, vegetates, changes colour, smokes, is inflamed, becomes obedient to the magnet, &c.; when the action of heat alone has been ascertained, it will be necessary to examine what further change takes place, by fusing it with various fluxes, and also whether it be capable of reduction to the metallic state.

The three most useful fluxes are, the triple phosphate of soda and ammonia, subcarbonate of soda, and borax. These are to be kept ready pulverised, and when used, a sufficient quantity may be taken up by the moistened point of a knife; the moisture causes the particles to cohere, and prevents their being blown away, when placed on the charcoal. The flux must be melted into a clear bead, and the substance then placed on it, and submitted, first to the action of the exterior, and then to that of the interior, flame. The appearances which ensue must be observed; as, 1st. If the substance be dissolved, and whether with or without effervescence. 2nd. The transparency, and colour of the glass whilst cooling. 3rd. The same circumstances, when cold. 4th. The nature of the glass formed by the exterior flame. 5th. Also, by the interior flame. 6th. The particular appearances with each of the fluxes.

Subcarbonate of soda does not form a bead on charcoal, but with a certain degree of heat is absorbed; it must therefore be added in very small quantities, and a gentle heat used at first, which will promote combination without the absorption of the alkali. Some minerals combine readily with very small portions of soda, but difficultly if more be added, and are absolutely infusible with it in great excess; and when the substance has no affinity for this flux, it is absorbed by the charcoal, and no combination ensues. When the mineral contains sulphur or sulphuric acid, the glass acquires a deep-yellow colour, which by the light of a lamp appears red, as if produced by copper. If the glass bead become opaque as it cools, so as to render the colour indistinct, it should be broken,

and a part of it mixed with more of the flux, till the colour becomes purer, and distinct. To make the colour more perceptible, the bead may be flattened whilst soft, or drawn-out to a thread.

If it be wished to *oxidate* a metallic substance, combined with either of the fluxes, the glass is first heated intensely, and when fused, gradually withdrawn from the point of the blue flame, and the operation repeated as often as necessary, using a jet of large aperture. The addition of a little nitre also assists the oxidation. For the *reduction* of metallic oxides, the glass bead is to be kept in fusion on charcoal, as long as it remains on the surface and is not absorbed, that the metallic particles may collect into a globule. It is then to be fused with an additional quantity of soda, which will be absorbed by the charcoal, and the spot where the absorption has taken place strongly ignited by a tube with a small aperture. By continuing the ignition, the portion of metal which was not previously reduced will now be brought to the metallic state, and the process may be assisted by placing the bead in a smoky flame, so as to cover it with a soot that is not easily blown off.

The beads which contain metals frequently have a metallic splendour, which is most easily produced by a gentle, fluttering, smoky flame, when the more intense heat has ceased. With a moderate heat the metallic surface remains; and by a little practice it may generally be known whether the substance under examination contains a metal or not. But the glass of borax alone sometimes assumes externally a metallic appearance. When the charcoal is cold, that part impregnated with the fused mass should be taken out with a knife, and ground with distilled water in an agate mortar. The soda will be dissolved; the charcoal will float, and may be poured off; and the metallic particles will remain in the water, and may be examined. In this manner most of the metals may be reduced.

The following table of the fusibility of the metals has been drawn up by Dr. Turner. (*Elements of Chem.*, p. 448.)

		Fahrenheit.		
Fusible below a red heat.	{	Mercury . . . . .	−39° Different Chemists.	
		Potassium . . . . .	136° } Gay Lussac and	
		Sodium . . . . .	190° } Thenard.	
		Tin . . . . .	442° } Crichton.	
		Bismuth . . . . .	497° } Klaproth.	
		Lead . . . . .	612° } Daniell.	
		Tellurium: rather less fusible than lead		
		Arsenic, undetermined . . . . .		
		Zinc . . . . .	773° Stromeyer.	
		Antimony, little below redness . . . . .		
		Cadmium . . . . .	442° Daniell.	
		Silver . . . . .	1873° } Daniell.	
		Copper . . . . .	1996° }	
		Gold . . . . .	2016° }	
Cobalt; rather less fusible than iron				
Iron, cast . . . . .	2786° Daniell.			
Iron, malleable	} require the highest heat } of a smith's forge.			
Manganese				
Nickel, nearly the same as cobalt				
Infusible below a red heat.	{	Palladium	} Almost infusible, and not to be procured in buttons by the heat of a smith's forge, but fusible before the oxyhydrogen blowpipe.	
		Molybdenum		
		Uranium		
		Tungsten		
		Chromium		
		Titanium		
		Cerium		
		Osmium		
		Iridium		
		Rhodium		
Platinum				
Columbium				

**ACTION OF OXYGEN.** When the metals are exposed at ordinary temperatures to the action of oxygen, or of common air, which produces analogous, though less powerful effects, they are very differently affected. If the gas be perfectly dry, few of them suffer any change, unless heated in it; they then lose their metallic characters, and form a very important series of compounds, the *metallic oxides*. A few of the metals resist the action of heat and air so completely, that they may be kept in fusion in an open crucible for many hours without undergoing change. This is the case with platinum and gold; hence they and a few others were called *noble* metals: by passing a strong electric discharge through them, when drawn into very fine wire, they are reduced to the state of impalpable powder, which is sometimes regarded as an oxide; but the appearance ensues in hydrogen as well as in common air, and the oxides of those metals are reducible by heat alone: the appearance, therefore, is probably referable to minute mechanical division only. Other metals readily absorb oxygen when exposed to a temperature approaching a red heat; as iron, mercury, nickel, &c.; others absorb it when in fusion, as lead, tin, antimony, &c.; others at lower, or even at common temperatures, as arsenic, manganese, sodium, potassium, &c. The mutual action, however, of metals and oxygen is apparently much interfered with by their aggregation, for some of them, which under ordinary circumstances are

only slowly oxidized by exposure to air and heat, are rapidly acted on when in very fine mechanical division, even at common temperatures; and this would probably be found more generally the case, had we the means of reducing them to extremely fine powder.

That the metals have different attractive powers in regard to oxygen is shown by the circumstance of one metal being oxidized at the expense of another: thus the oxide of mercury, heated with metallic iron, produces metallic mercury and oxide of iron; potassium, heated with oxide of manganese, becomes oxidized, and metallic manganese is obtained. Upon the same principle, solutions of metallic oxides in the acids may often be reduced to the metallic state by the immersion of other metals. Mercury thus decomposes nitrate of silver; copper decomposes nitrate of mercury; and iron decomposes nitrate of copper. In these cases of metallic precipitation, electricity becomes active the moment that the deposition commences; the precipitating or reducing metal being positive, and that which is precipitated, or reduced, negative. Very beautiful crystalline deposits may thus often be obtained, as where silver is precipitated by mercury, and lead by zinc. Metals which are thus difficultly thrown down from their solutions in acids, are sometimes easily obtained from their solutions in alkalis, as for instance tungsten and tin.

Many of the metallic oxides are reduced, when in solution, by the protosalts of iron and tin, which by abstracting oxygen pass into the state of persalts, and throw down the reduced metal in a pulverulent form. The protosalts of iron are in these cases preferable to those of tin, inasmuch as the resulting peroxide of iron is retained in solution, and the precipitated metal is pure; but the peroxide of tin often falls along with the reduced metal, in consequence of its difficult solubility in most of the acids.

Some of the oxides are decomposed by mere exposure to heat, as those of platinum, gold, silver, and mercury: others require the joint action of heat, and some substance having a high attraction for oxygen, such as charcoal. Thus when oxide of lead is heated with charcoal, carbonic acid gas is evolved, and metallic lead obtained. This important process is termed *reduction*, and is performed in various ways, as will appear by reference to the history of individual metals. The reduction of an oxide is also frequently effected by passing a current of dry hydrogen over it in a heated tube; in this case the oxygen is carried off in the form of water. Sometimes the reduction of an oxide is effected by the aid of another metal possessed of a very superior attraction for oxygen, as in the cases cited in the preceding paragraph; and in some cases complicated attractions are directed to the process of reduction, as in the production of potassium by the action of red-hot iron upon hydrate of potassium.

Electricity is an all-powerful agent in metallic reduction, and capable, under certain circumstances, of overcoming the most energetic attractions. This important subject has been discussed and illustrated in a former chapter (p. 280).

Some of the metallic combinations, especially those of gold, are reducible by the agency of *light* (p. 184); the salts of silver are also discoloured or partially reduced by the same agency.

The oxidizement of a metal is an essential preliminary to the forma-



tion of its oxy-salts, or, in other words, to its combinations with oxy-acids; and in this respect common chemical nomenclature is inaccurate. Thus we speak of sulphate of *copper*, nitrate of *zinc*, &c., meaning sulphate of *oxide* of copper, nitrate of *oxide* of zinc, &c. This ambiguity is prevented with respect to the alkalies and alkaline earths, the oxides of their bases being characterized by a distinct termination: thus phosphate of *soda* means phosphate of *oxide of sodium*, &c.; a circumstance which induced Sir H. Davy to propose an analogous termination for all the oxides, appropriately applied to their common Latin names: *Cuprà*, oxide of copper; *Argenta*, oxide of silver, &c.; but this proposal, which he extended to other compounds, was never generally adopted.

Each metal has a certain definite quantity of oxygen with which it combines; and where the same metal unites in more than one proportion with oxygen, in the second, third, and other compounds, it is a multiple of that in the first, consistent with the law of definite proportionals. Thus, 100 parts of mercury combine with 4 of oxygen to produce the black oxide, and with 8 to produce the red oxide. Copper also forms two oxides; in the one 12.5 of oxygen are united to 100 of metal, and in the other to 25. Where two oxides only are thus formed, that with the minimum of oxygen is termed the *protoxide*, and that with the maximum of oxygen the *peroxide*; where there are three or four distinct steps of oxidizement, the terms *deutoxide* or *binoxide*, and *tritoxide* or *teroxide*, may be applied to the second and third stages; and where the proportion of oxygen, in three oxides, is in the relation of 1,  $1\frac{1}{2}$ , and 2, the second is termed a *sesquioxide*.

M. F. de Montizon has attempted to show (*Ann. de Chim. et Phys.*, vii., 7) that a relation subsists between the quantity of oxygen with which the metals combine, and their specific gravities; the oxygen being a multiple or submultiple of the density; and he has given a table comparing the results deduced from such a theory, with those obtained by analysis; his instances, however, do not establish the conclusion.

Among the combinations of metals with oxygen, some are insoluble in water, or nearly so, and have neither taste nor smell; others are soluble and sour, constituting the *metallic acids*; others are soluble and alkaline, forming the *fixed alkalis* and *alkaline earths*. They are of all colours, and frequently the same metal united to different proportions of oxygen produces compounds differing in colour: thus we have the *black* and *red* oxide of mercury, the *green* and the *black* oxide of manganese, &c.

The different oxides of the same metal frequently form distinct salts with the acids, and the quantity of acid required to neutralize the oxide bears a direct proportion to the oxygen which it contains. Thus, 208 parts of protoxide of mercury, containing 8 of oxygen, combine with 40 of sulphuric acid to form the *protosulphate of mercury*; and 216 parts of the peroxide of mercury require 80 of sulphuric acid to constitute the *persulphate of mercury*. This law was first developed by Gay Lussac (*Mémoires d'Arcueil*, ii., 159). It sometimes happens that the same oxide unites with an acid in two proportions, forming two distinct salts, in which case the acid in the second is a multiple of that in the first. Thus, 48 parts of potassa unite to 22 and to 44 of carbonic acid, forming

a *carbonate* and a *bicarbonate* of potassa. We thus have an *oxalate*, a *binoxalate*, and a *quadroxalate*, of potassa, &c.

The metallic oxides occasionally combine with each other, forming definite compounds; instances of such combinations are common in the mineral kingdom: in this case one of the oxides appears to perform the part of an acid, and the other that of base. Many of the compounds of silica furnish illustrative instances. The salts of the proper metallic acids are also analogous compounds.

**ACTION OF CHLORINE\*.** All the metals appear susceptible of combining with chlorine, and of producing a class of compounds which may be termed *metallic chlorides*. There are a few of the metals which resist the action of chlorine at common temperatures, but when heated they all combine with it; some slowly; others rapidly, and with intense ignition. Copper-leaf, powdered antimony, arsenic, &c., burn when thrown into the gas: mercury and iron inflame when gently heated in it; silver and platinum, quietly absorb it. In these cases, minute mechanical division remarkably accelerates the action. The attraction of chlorine for metals is, with very few exceptions, greater than that of oxygen; consequently, when a metallic oxide is heated in chlorine, oxygen is evolved, and a chloride formed. The insoluble chlorides are also formed by adding solution of chlorine, or of the soluble chlorides, or of muriatic acid, to the soluble metallic salts. Thus chloride of silver, which is insoluble, is thrown down from the soluble nitrate of silver by solution of chlorine, of muriatic acid, and of common salt: hence, too, all the soluble chlorides are recognised, by yielding a white precipitate in solution of nitrate of silver, which is soluble in ammonia, and which, when pure, rapidly blackens by exposure to the sun's rays.

The physical and chemical properties of the chlorides are extremely various. They are nearly of all colours. They are generally unchanged

\* The compounds of chlorine, iodine, bromine, and fluorine, which we have here designated *chlorides*, *iodides*, &c., have been formed by Berzelius and some other writers into a distinct class, designated *haloïde salts*; by others they are designated *salts of the hydracids*, as opposed to the *salts of the oxyacids*; but I have not thought the value of such distinctions sufficient to induce me to infringe upon the *general order of arrangement* adopted in this Manual. The difference, however, in the constitution and peculiarities of the hydracids and their salts must not be overlooked: these acids are marked by the absence of oxygen, and by the union of their elements in one proportion only; so that one volume of each of their components combine to produce two volumes of the respective hydracids. The question how far hydrogen is essential to the developement of acid properties has been elsewhere adverted to. It is also to be remarked, that certain

compound bases perform, as it were, the part of simple substances in constituting acids, especially with hydrogen: this is the case with cyanogen, which thus forms hydrocyanic acid; and with sulpho-cyanogen, which forms sulpho-cyanic acid; and the action of the metals upon these acids corresponds in many instances to their action upon those with simple bases; potassium, for instance, when it acts upon one volume of hydrocyanic acid disengages half a volume of hydrogen, and combines with the cyanogen, to form what we have termed *cyanuret of potassium*; from sulpho-cyanic acid it also disengages hydrogen, and a *sulpho-cyanuret of potassium* is the result. The termination *uret* is here employed consistently with the nomenclature applied to the simple combustibles; but others, pursuing the analogy to chlorine, &c., just mentioned, have called these compounds *cyanides*, *sulpho-cyanides*, &c.

by heat; but some undergo decomposition. Some are soluble, others insoluble, in water. Some permanent; others deliquescent. Several of them decompose water, giving rise to the formation of muriatic acid, and an oxide; or, perhaps, in some cases to a muriate. They are fusible, and many of them crystallizable. Some are extremely volatile at common temperatures, and others fixed in high heats. A few exist, at all ordinary temperatures, in the liquid state. They are generally decomposed at a red heat by hydrogen, which produces muriatic acid, and reduces the metal. Anhydrous sulphuric acid appears not to act upon them; but the common hydrated acid decomposes them, with few exceptions, evolving muriatic acid: the theory of these changes is elsewhere explained. Some of the metals rapidly decompose certain chlorides in consequence of their superior attraction: thus chloride of silver is decomposed by zinc, &c. All the soluble chlorides furnish a white precipitate in solution of nitrate of

The same metal often forms more than one compound with chlorine, and these compounds are designated as the oxides. Thus we have the *protochloride* and *perchloride* of mercury, &c.

Many of the metals decompose muriatic acid, in which case hydrogen is evolved, and a metallic chloride produced; and when metallic oxides are heated in muriatic acid, they generally give rise to the formation of a chloride and water.

There are a few metallic oxides which, at low temperatures, absorb and retain chlorine, but they hold it by very feeble attraction. The chlorides of potassa and of lime will be described under those bodies. It has also been combined with the oxides of iron, zinc, and copper. (Grouvelle, *Ann. de Chim. et Phys.*, xvii.) These compounds are decomposed by heat and by the acids.

**ACTION OF CHLORIC ACID.** The compounds of the metallic oxides with chloric acid, or *chlorates*, are decomposed by heat with the copious evolution of oxygen, and a chloride generally remains: they deflagrate when heated with charcoal or other combustibles. In the chlorates the proportion of oxygen in the base to that in the acid is as 1 to 5: some of these salts have been long known, others only recently investigated. The *oxychlorates*, or *perchlorates*, have been scarcely examined. Like the chlorates, they yield oxygen when heated: and the proportion of oxygen in the base to that in the acid is as 1 : 7.

**ACTION OF IODINE.** Iodine, aided by heat, acts upon many of the metals, and produces *metallic iodides*. Some of these are soluble in water without decomposition; others decompose water and produce *hydriodates*; others are insoluble. The insoluble iodides may generally be formed by adding a solution of iodine or of hydriodic acid, or of an iodide, to the soluble metallic salts. Iodine often combines in more than one proportion with metals, forming a *protiodide* and a *periodide*. The iodides are decomposed by chlorine and bromine, and some by oxygen; but in other instances iodine expels oxygen from its combinations with the metals. Iodides are also decomposed by nitric and by sulphuric acid; and in all these cases the free iodine is easily recognised by starch: (p. 341.) According to Gay Lussac, when the vapour of iodine is passed over hot lime, baryta, and strontia, it does not expel their oxygen, but unites with them as oxides.

These compounds are not very permanent, and are decomposed at a temperature a little exceeding that required to form them.

**ACTION OF IODIC ACID.** The compounds of this acid with the metallic oxides have been but little examined: they are decomposed and converted into iodides by heat, sometimes with the evolution of oxygen only; at others, iodine is also given off.

**ACTION OF BROMINE.** Bromine combines with the metals and produces *bromides*, analogous in their general habitudes, to the chlorides and iodides; they are formed either by the direct action of bromine, or by that of hydrobromic acid upon metallic oxides; or, when insoluble, they are precipitated by the addition of the soluble bromides to metallic solutions. Bromine also unites to some of the metallic oxides, and produces bleaching compounds. Chlorine disengages bromine from its binary metallic compounds, and bromine expels iodine from the iodides; so that the attraction of bromine for the metals is intermediate between chlorine and iodine.

The *Bromates* are little known. When heated to redness they become *bromides*, by the loss of oxygen.

**ACTION OF FLUORINE.** As fluorine has not been obtained in a separate state, its immediate action upon the metals is not known; but it would probably be energetic. Such of the *fluorides* as are insoluble may be obtained by the medium of a solution of fluoride of potassium, or by precipitation by hydrofluoric acid: the soluble fluorides are formed by digesting the oxides in the hydrofluoric acid. The fluorides are not decomposed by oxygen, chlorine, iodine, or bromine; but they are immediately recognised by the evolution of hydrofluoric acid, when moistened and heated with sulphuric acid, and by their action upon glass under such circumstances.

**ACTION OF HYDROGEN.** Hydrogen forms permanent compounds with two of the metals only, namely, arsenic and tellurium. It appears to combine with each in two proportions, forming two solid compounds, the *hydrurets* or *hydrogurets* of arsenic and tellurium; and two gaseous compounds, *arseniuretted* and *telluretted hydrogen*. At high temperatures it dissolves potassium, forming *potassiuretted hydrogen gas*. Hydrogen also appears to combine with zinc, at least it frequently retains a little of that metal in its gaseous state.

There are many of the metallic oxides and chlorides, which are decomposed by hydrogen: the oxides are reduced with the formation of water, and the chlorides with the production of muriatic acid.

**ACTION OF WATER.** Those metals which are speedily acted upon by common air and oxygen, are also generally capable of decomposing water; some of them rapidly, others slowly. There are some metals which are not acted upon by air deprived of moisture, nor by water deprived of air; but moist air, or water containing air, effect their oxidization: this appears to be the case with iron. (Dr. Marshall Hall, *Quarterly Journal*, vii., 55.) Water combines with some of the metallic oxides, and produces *hydrated oxides*, or *metallic hydrates*. In these the relative proportion of water is definite. Some are easily decomposed by very moderate heat, as hydrate of copper; others retain water even when

heated to redness, as hydrate of potassa; others are decomposed at a red heat, as hydrate of lime.

**ACTION OF NITRIC ACID.** The greater number of metals are capable of decomposing nitric acid by the abstraction of a part of its oxygen, and thus of resolving it into some of the other nitric compounds; nitric acid is a very generally acting solvent, therefore, of these bodies. It dissolves nearly all the metallic oxides, and produces a numerous class of *nitrates*, which, if prepared with heat and with excess of acid, generally contain the metal at its maximum of oxidizement. The nitrates are all decomposed by a red-heat; they give off oxygen and nitrogen, either separate or combined, and the metallic oxide remains. They are also decomposed when heated with sulphur, phosphorus, or charcoal; and sulphurous, phosphoric, and carbonic acids are formed: the phosphoric, being a fixed acid, remains united to the metallic oxide; while the sulphurous and carbonic acids are usually expelled. The nitrates are decomposed by sulphuric acid, nitric acid is evolved, and *sulphates* are formed. In the neutral nitrates the proportion of oxygen in the acid is to that in the base as 5 to 1. Thus in the nitrate of potassa, 48 parts of potassa, containing 8 of oxygen, are combined with 54 of nitric acid, containing 40 ( $8 \times 5$ ) of oxygen; and in the nitrate of oxide of copper, 40 parts of oxide of copper, containing 8 of oxygen, are combined with 54 of nitric acid, containing 40 of oxygen.

**ACTION OF AMMONIA.** At high temperatures some of the metals are capable of decomposing ammonia. Liquid ammonia dissolves several of the metallic oxides, and with some of them forms crystallizable compounds. It dissolves the oxides of silver, copper, zinc, arsenic, antimony, and tellurium; the protoxides of iron, cobalt, and nickel; and the peroxides of tin, mercury, gold, and platinum. These compounds are all decomposed by heat. The compounds of ammonia with the oxides of gold, silver, and platinum, detonate when heated, and the oxide and the ammonia are both decomposed.

**ACTION OF SULPHUR.** All the metals appear capable of forming *sulphurets*. These are formed, 1st, By heating the metal in a close vessel, with sulphur; and it not unfrequently happens that, during the combination, the metal becomes intensely ignited, burning as it were in the vapour of the sulphur, and furnishing a striking instance of combustion without the presence of oxygen; this is the case with potassium and sodium, and with the filings or shavings of copper, lead, and iron. 2ndly, By heating a mixture of sulphur and a metallic oxide, in which case sulphurous acid escapes, and the metallic sulphuret remains behind. 3rdly, By decomposing the *sulphates*, either by subjecting them to the action of a current of hydrogen gas in a heated tube, or by heating a mixture of the sulphate with charcoal. 4thly, By the action of sulphuretted hydrogen. 5thly, By fusing the oxide with a mixture of carbonate of potash and sulphur, in which case an alkaline bisulphuret is first formed, and sustains a red heat, but at that temperature a proportion of its sulphur is imparted to the reduced metal of the oxide. The sulphurets are in general brittle; some have a metallic lustre, and are opaque; others are without lustre, and more or less transparent. They are fusible. Some are soluble, but the greater number insoluble in water. Where the

same metal forms two sulphurets, the sulphur in those containing the largest proportion is an exact simple multiple of the sulphur in those containing the smallest proportion; hence we have *sulphurets* and *bisulphurets*. There are also metallic *sesquisulphurets*; and, generally speaking, the sulphurets correspond in number and atomic composition with the oxides. When the metallic sulphurets are heated in close vessels, some undergo no change, as those of sodium and potassium; others sublime unaltered, as sulphuret of mercury and sulphuret of arsenic; others lose a portion of their sulphur, and, if air be admitted, sulphurous acid escapes, and the metal passes into the state of oxide, as sulphuret of lead and sulphuret of copper; and it is thus that these sulphurets are oxidized by the process called *roasting*, previous to their reduction, upon the large scale; others again are entirely decomposed, the metal being completely reduced; this happens on heating sulphuret of platinum or of gold. Definite compounds of sulphur with some of the metallic oxides, have been obtained by Arfwedson. (*Ann. de Chim. et Phys.*, vi., 204.)

There are certain double sulphurets, which Berzelius has designated *sulphur salts*; in these cases he terms the electronegative sulphurets, *sulphur acids*; and the electropositive sulphurets, *sulphur bases*; among the *sulphur acids*, he enumerates the sulphurets of arsenic, antimony, gold, molybdenum, tellurium, tin, and tungsten; he also calls sulphuretted hydrogen, sulphocyanic acid, sulphuret of selenium, and sulphuret of carbon, *sulphur acids*. The principal *sulphur bases* are the proto-sulphurets of the metals of the alkalis and alkaline earths, and the hydro-sulphuret of ammonia (sulphuret of ammonium.)

HYPOSULPHUROUS ACID combines with the metallic oxides, and produces a class of salts termed *hyposulphites*. Several of these have been examined by Herschel. (*Edin. Phil. Journal*, i.) In some of their characters they resemble the sulphites: they are easily soluble; of a bitter or sweet taste; and decomposed by a heat below redness, and by almost all other acids. Their solutions readily dissolve chloride of silver.

SULPHUROUS ACID combines with many of the metallic oxides, producing *sulphites*; in some instances oxygen is transferred from the oxide to the acid, and sulphates result.

The *sulphites* are soluble in water, and have a sulphurous taste and smell. Exposed to moist air, they absorb oxygen, and pass into the state of sulphates. They are decomposed by sulphuric acid, which expels sulphurous acid, and the salts are converted into sulphates. When perfectly pure they are not affected by solution of baryta.

HYPOSULPHURIC ACID forms with the metallic oxides a class of *hyposulphates*. They do not afford precipitates with solution of baryta. When heated they evolve sulphurous acid, and are converted into neutral sulphates: when their solutions are boiled with sulphuric acid, sulphurous acid is evolved, but no sulphur is precipitated.

SULPHURIC ACID, in its concentrated state, and unaided by heat, is acted upon by a few of the metals only; when diluted, some of them are oxidized at the expense of the water, hydrogen is evolved, and the metallic oxide combines with the acid, producing a *sulphate*. In these cases the hydrogen evolved is the indicator of the quantity of oxygen transferred to the

metal; every volume of hydrogen is the equivalent of half a volume of oxygen, and accordingly the production of 100 cubic inches of hydrogen indicates the transfer of 50 of oxygen, or, by weight, of about 17 grains. As different metals unite to different weights of oxygen, they will obviously evolve different quantities of hydrogen. Thus, if one metal, to become soluble in sulphuric acid, require to be united with 10, and another with 20 per cent. of oxygen, the latter will evolve twice the volume of hydrogen, compared with the former. As the evolution of hydrogen, during the solution of a metal in dilute sulphuric acid, is referable to its oxidizement, no hydrogen will be evolved by the action of the acid upon an oxide, but it will be merely dissolved.

The sulphates are an important class of salts. The greater number of them are soluble in water, and the solutions yield a precipitate with the soluble salts of baryta which is insoluble in acids and alkalis. The insoluble sulphates may be recognised by igniting them in fine powder with thrice their weight of carbonate of soda, by which a soluble sulphate of soda is formed: it may be separated by water and filtration, and tested by nitrate of baryta. The sulphates of potassa, soda, lithia, lime, baryta, and strontia, resist a white heat without decomposition: the other sulphates evolve, when intensely heated, sulphuric acid, sulphurous acid, and oxygen. Many of them are decomposed at high temperatures by the action of hydrogen, which carries off the oxygen of the acid, and of the base, and leaves a metallic sulphuret. In some cases the sulphur also combines with the hydrogen, and the sulphate thus affords a reduced metal. They are all decomposed at a red heat by charcoal, and most of them are thus converted into sulphurets; carbonic acid, and carbonic oxide, being at the same time evolved. In the neutral sulphates the proportion of oxygen in the acid is to that in the base as 3 to 1. Thus sulphate of soda is composed of 32 soda, containing 8 of oxygen, combined with 40 of sulphuric acid, containing 24 ( $8 \times 3$ ) of oxygen; and in the sulphate of copper, 40 parts of oxide of copper, containing 8 of oxygen, are combined with 40 of sulphuric acid, containing 24 ( $8 \times 3$ ) of oxygen.

**ACTION OF SULPHURETTED HYDROGEN.** When sulphuretted hydrogen combines with metallic sulphurets, it forms one class of the *sulphur-salts*. It seems doubtful whether any of the metals combine with sulphuretted hydrogen. Its combinations with their oxides have been termed *hydrosulphates* or *hydrosulphuretted oxides*, but it generally happens that in the mutual action of the sulphuretted hydrogen and the oxide, both are decomposed, the hydrogen combining with the oxygen of the oxide to form water, and the sulphur uniting to the metal to form a metallic sulphuret. In a few cases the metallic oxide is reduced. The following table shows the effect of sulphuretted hydrogen and of sulphuretted hydrosulphuret of ammonia upon solutions of several of the metals, as far as *colour* of the precipitate is concerned, these precipitates being often resorted to as qualitative tests.

METAL.	SOLUTION.	SULPHURETTED HYDROGEN.	HYDROSULPHURET OF AMMONIA.
MANGANESE	Neutral protochloride	No precipitate	Copious ochre-yellow
IRON	Neutral protosulphate	Blackish and small in quantity	Black and abundant
Ditto	Perchloride	Abundant black	Black
ZINC	Chloride	A little opalescent and then milky	Straw-colour and copious
TIN	Acid protochloride	Brown	Deep orange
Ditto	Acid perchloride	At first 0, then yellow and copious	Apple-green
CADMIUM	Chloride	Yellow	Yellow
COPPER	Protochloride	Deep brown	Brown
Ditto	Nitrate	Black	Brown and black
LEAD	Chloride and nitrate	Black	Brown and black
ANTIMONY	Tartrate of antimony and potassa.	Deep orange-red	Bright orange
BISMUTH	Tartrate of bismuth and potassa.	Deep brown	Deep brown
COBALT	Chloride	0 but blackish	Copious black
URANIUM	Sulphate	Brown	Blackish brown
TITANIUM	Acid muriate	0	Black
Ditto	Neutral sulphate	0	Green
CERIUM	Protosalts	0	White
TELLURIUM	Sulphate	Black	Black
ARSENIC	White oxide (acid sol.)	Yellow	Yellow
Ditto	Arsenic acid (ditto)	Ditto	Ditto
NICKEL	Sulphate	Brown	Black
MERCURY	Acid nitrate	Black, then gray, and black by excess of test	Black by excess of test
Ditto	Acid pernitrate	Ditto	Ditto
Ditto	Corrosive sublimate	Brown by excess of test	Ditto
OSMIUM	Solution of oxide	Metallic	Metallic
PALLADIUM	Muriate	Brown	Brown
SILVER	Nitrate	Black and metallic	Ditto
GOLD	Chloride	Black and reduced gold	Yellow
PLATINUM	Chloride	Deep brown	Pale brown

**ACTION OF SELENIUM.** Selenium acts upon the metals with nearly the same phenomena as sulphur, and in their general characters the *seleniurets* and sulphurets are analogous: when heated in the open fire the selenium burns slowly off with an azure flame, and the odour of radish. The atomic composition of the seleniurets follows that of the sulphurets, and they are best obtained by precipitating the metallic solutions with seleniuretted hydrogen, and then, if biseleniurets are required, the precipitate may be fused with selenium, and the excess driven off by distillation. The *selenites* and *seleniates* are decomposed by sulphurous acid, which throws down the selenium of a red colour in the cold, and nearly black at a boiling heat. Distilled with muriate of ammonia, selenium passes over. In the selenites the oxygen in the acid is to that in the base as 2 to 1, and in the seleniates as 3 to 1; these salts, therefore, are isomorphous with the sulphites and sulphates.

**ACTION OF PHOSPHORUS.** Phosphorus combines with the greater number of the metals, forming a series of *metallic phosphurets*. There are three methods of forming them; either by heating a mixture of phos-



phorus and the metal, or projecting phosphorus upon the metal previously heated to redness; or by heating a mixture of the metal or its oxide, with phosphoric acid and charcoal; or by passing phosphuretted hydrogen over the heated metallic oxide. A few only of the phosphurets can be obtained in the humid way, for when metallic solutions are precipitated by phosphuretted hydrogen the metal is generally reduced. These phosphurets have a metallic lustre; if they contain a difficultly fusible metal, they are more fusible than the metal they contain; if an easily fusible metal, less so. They are mostly crystallizable, and totally or partly decomposable at a high temperature. The greater number of the phosphurets have only been examined by Pelletier. (*Ann. de Chim.* tom. i. and xiii., and *Mémoires et Observations de Chimie.*) The existence of compounds of metallic oxides with phosphorus appears doubtful.

When phosphorus is introduced into the solutions of those metals which have but a feeble attraction for oxygen, it reduces them to the metallic state. Thus, gold, silver, and platinum are thrown down by immersing a stick of phosphorus into their respective solutions.

The *Hypophosphites* and the *Phosphites* have been imperfectly examined. When heated they evolve phosphorus or phosphuretted hydrogen, and are converted into phosphates: their solutions smell of phosphorus, and reduce the salts of gold, silver, and mercury.

**ACTION OF PHOSPHORIC ACID.** The *metallic phosphates*\* may be formed either by dissolving the oxides in phosphoric acid, or by adding a solution of phosphoric acid, or of an alkaline phosphate, to solutions of those metals which form insoluble or difficultly soluble phosphates. The greater number of the phosphates are decomposed and converted into phosphurets, by ignition with charcoal; and those containing volatile oxides are volatilized at high temperatures. The phosphates of ammonia, potassa, and soda, are soluble; but the greater number of these salts are difficultly soluble, and some insoluble in water: they are dissolved by phosphoric, nitric, and muriatic acids, and precipitated, generally without change, by ammonia. Those which are insoluble are mostly decomposed by boiling with carbonate of potassa. Several of the phosphates occur in the native state, constituting some beautiful but generally rare minerals.

In the neutral phosphates the quantity of oxygen in the acid is to that in the base as 2.5 to 1. Thus, phosphate of soda consists of 32 soda containing 8 oxygen, and 36 phosphoric acid containing 20 ( $8 \times 2.5$ ) of oxygen. But the phosphoric acid unites to bases in several other proportions, giving rise to a variety of subsalts and supersalts, of which the most important will be noticed in the sequel.

**ACTION OF CARBON.** Carbon unites to very few of the metals; and of the metallic *carburets*, one only is of importance, namely, carburet of iron, which constitutes the varieties of cast-iron, and steel.

When some of the metallic cyanurets, and certain of the salts of metallic oxides and organic acids are decomposed by heat, the residuary products appear to be, in some cases, true carburets; these, however, have been but imperfectly examined.

\* The isomeric varieties of these salts, namely, the *pyrophosphates* and *metaphosphates* will be pointed out afterwards.

CARBONIC ACID unites with the greater number of the metallic oxides, and forms *carbonates*, of which the distinctive characters have already been noticed; most of them are of difficult solubility, and may be formed by adding an alkaline carbonate to the metallic solution. Of the carbonates some are entirely, and others only partially, decomposed at a red heat. Carbonate of magnesia, for instance, loses the whole of its carbonic acid at a red heat; carbonate of potassa retains it; and bicarbonate of potassa loses one-half, and passes into the state of carbonate. The carbonates are decomposed by nearly all the other acids, and are then distinguished by the effervescence that ensues on the escape of carbonic acid gas.

In the neutral carbonates the proportion of oxygen in the base is to that in the acid as 1 to 2. Carbonate of potassa, for instance, consists of 48 of potassa containing 8 of oxygen, and 22 of carbonic acid, containing 16 ( $8 \times 2$ ) of oxygen.

The carbonates are not uncommon natural products.

CYANOGEN combines with many of the metals, and forms compounds, which we call *cyanurets*, or *cyanides*. The compounds of the *cyanic acid*, or the *cyanates*, are so decomposed, either by the action of water or the acids, that the cyanic acid is resolved into carbonic acid and ammonia, with no trace of hydrocyanic acid. The *fulminates* explode when heated, and evolve hydrocyanic acid by the action of the oxyacids. The *Hydrocyanates* have been but imperfectly examined; they appear peculiarly susceptible of decomposition.

*Sulphocyanurets and Sulphocyanates* produce a characteristic red colour when added to a solution of persulphate of iron.

THE ACTION OF BORON upon the metals has not been fully investigated.

The BORATES of the alkalis are soluble: with other bases the boracic acid mostly forms difficultly soluble or insoluble compounds, which are easily formed by adding solution of boracic acid, or a soluble borate to the metallic solution. The borates are generally decomposed in the humid way, by sulphuric, nitric, and muriatic acids; but, at a red heat, the boracic acid expels the more volatile acids from their basic compounds. The presence of this acid may in many instances be detected by digesting its compounds in sulphuric acid, evaporating to dryness, and boiling the residue in alcohol, which will then be found to burn with the characteristic green flame.

ACTION OF THE METALS UPON EACH OTHER. The metals may, for the most part, be combined with each other, forming a very important class of compounds, the *metallic alloys*. In the act of combination they generally evolve heat; thus, when platinum and tin-foil are fused together, there is vivid ignition; so, also, when melted zinc and copper are suddenly mixed in the proportions to form brass, the increase of heat is such as to vaporize part of the metal. Various processes are adopted in the formation of alloys, depending upon the nature of the metals. Many are prepared by simply fusing the two metals in a covered crucible; but if there be a considerable difference in the specific gravity of the metals, the heavier will often subside, and the lower part of the bar or ingot will differ in composition from the upper; this may

be to a great extent prevented by agitating the alloy till it solidifies. Mr. Hatchett found that when an alloy of gold and copper was cast into bars, the moulds being placed perpendicularly, the upper part of the bar contained more copper than the lower (*Phil. Trans.* 1803); and although copper and silver appear readily to combine, it is extremely difficult to form a bar of their alloy, of perfectly uniform composition throughout.

Where one of the metals is very volatile, it should generally be added to the other after its fusion; and if both metals be volatile, they may be sometimes united by distilling them together.

It has been a question whether alloys are to be considered as compounds, or as mere mixtures; but, in many cases, their properties leave little doubt of their being real compounds, and in some cases they are found to unite in definite proportions only; and it is not improbable that all the alloys contain definite compounds of the metals. It is observed by Berzelius, that the acidifiable metals have the greatest tendency to combine with those which produce salifiable bases, and that arsenic, antimony, and tellurium, form definite compounds analogous to sulphurets and phosphurets, which are not uncommon as ores. Among the artificial, as well as the natural alloys, there are many which are crystallizable, and the true compound may sometimes be separated from the mere mixture of the metal by its tendency to crystallize.

The principal characters of the alloys are the following:—i. We observe a change in the ductility, malleability, hardness, and colour. Malleability and ductility are usually impaired, and often in a remarkable degree: thus gold and lead, and gold and tin, form a brittle alloy. The alloy of copper and gold is harder than either of its component parts; and a minute quantity of arsenic added to copper renders it white.—ii. The specific gravity of an alloy is rarely the mean of its component parts, in some cases an increase, in others a diminution of density having taken place, as shown by the following Table from Thenard.—*Traité de Chimie*, vol. i., p. 394.

Alloys possessed of greater specific gravity than the mean of their components.

Gold and Zinc.  
 „ Tin.  
 „ Bismuth.  
 „ Antimony.  
 „ Cobalt.  
 Silver and Zinc.  
 „ Lead.  
 „ Tin.  
 „ Bismuth.  
 „ Antimony.  
 Copper and Zinc.  
 „ Tin.  
 „ Palladium.  
 „ Bismuth.  
 „ Antimony.  
 Lead and Bismuth.  
 „ Antimony.  
 Platinum and Molybdenum.  
 Palladium and Bismuth.

Alloys having a specific gravity inferior to the mean of their components.

Gold and Silver.  
 „ Iron.  
 „ Lead.  
 „ Copper.  
 „ Iridium.  
 „ Nickel.  
 Silver and Copper.  
 Copper and Lead.  
 Iron and Bismuth.  
 „ Antimony.  
 „ Lead.  
 Tin and Lead.  
 „ Palladium.  
 „ Antimony.  
 Nickel and Arsenic.  
 Zinc and Antimony.

iii. The fusibility of an alloy is generally greater than that of its components. Thus platinum, which is infusible in our common furnaces, forms, when combined with arsenic, a very fusible alloy; and an alloy of certain proportions of lead, tin, and bismuth, is fusible at  $212^{\circ}$ , a temperature many degrees below the melting-point of its most fusible constituent.

iv. Alloys are generally more oxidizable than their constituents, taken singly; a property which is, perhaps, partly referable to the formation of an electrical combination. Where an alloy consists of two metals, the one easily and the other difficultly oxidizable, it may be decomposed by exposing it to the action of heat and air, the former metal being converted into an oxide; its last proportions, however, are often not easily separated, being protected by combination with the least oxidizable metal. An alloy of three parts of lead and one of tin is infinitely more oxidizable than either of its components, and easily burns at a dull-red heat.

v. The action of acids on alloys may generally be anticipated by a knowledge of their effects upon the constituent metals; but if a soluble metal be alloyed with an insoluble one, the former is often protected by the latter from the action of an acid. Thus, silver alloyed with a large quantity of gold, resists the action of nitric acid in consequence of the insolubility of the latter metal in that acid; and, in order to render it soluble, it is requisite that it should be made to form about a fourth part of the alloy, in which case the nitric acid extracts it, and leaves the gold in an insoluble film or powder.

In other cases a metal insoluble, or nearly so, in certain acids, *per se*, is taken up in considerable quantity when alloyed; thus, platinum is insoluble in nitric acid, but its alloy with silver is to a certain extent soluble; and when a triple alloy of gold and silver with a little platinum is rolled out and digested in nitric acid, both the silver and the platinum are taken up. Rhodium is insoluble in acids, but, when alloyed with copper or lead, the nitromuriatic acid dissolves it.

Various classifications of the metals have been adopted by chemical authors\*, some dependent upon their *physical*, others upon their *chemical* properties. The former can scarcely be considered as adapted to chemical

\* Berzelius divides the metals into two leading classes: 1. Bases of the alkalis and earths; 2. Bases of the oxides and acids. The former are distinguished by their low specific gravity, being either lighter, or but little heavier than water, and they are so easily oxidized as to decompose water at common temperatures: in this list he includes Kalium (Potassium,) Natrium (Sodium,) Lithium, Ammonium, (the hypothetical base of ammonia,) Barium, Strontium, Calcium, Magnium (Magnesium,) Alumium, Beryllium (Glucinum,) Yttrium, and Zirconium. The second class he subdivides into, 1. Electronegative metals; that is, such as in combination with oxygen have a greater tendency to form acids, than oxides or salifiable bases: these are, Selenium? Arsenic, Chromium, Molybdenum, Wolframium (Tungsten,) Antimony, Tellurium, Tantalium (Columbium,) Titanium, Osmium, and Gold. 2. Electropositive metals, or such as in combination with oxygen especially produce salifiable bases: these are Platinum, Iridium, Rhodium, Palladium, Silver, Mercury, Uranium, Copper, Bismuth, Tin, Lead, Cadmium, Zinc, Nickel, Cobalt, Iron, Manganese, Cerium. The metals of the two last divisions are all more than four times heavier than water, very few of them are oxidized at common temperatures either by air or water, and their oxides are reduced by charcoal at high temperatures, and by potassium, at a moderate heat.

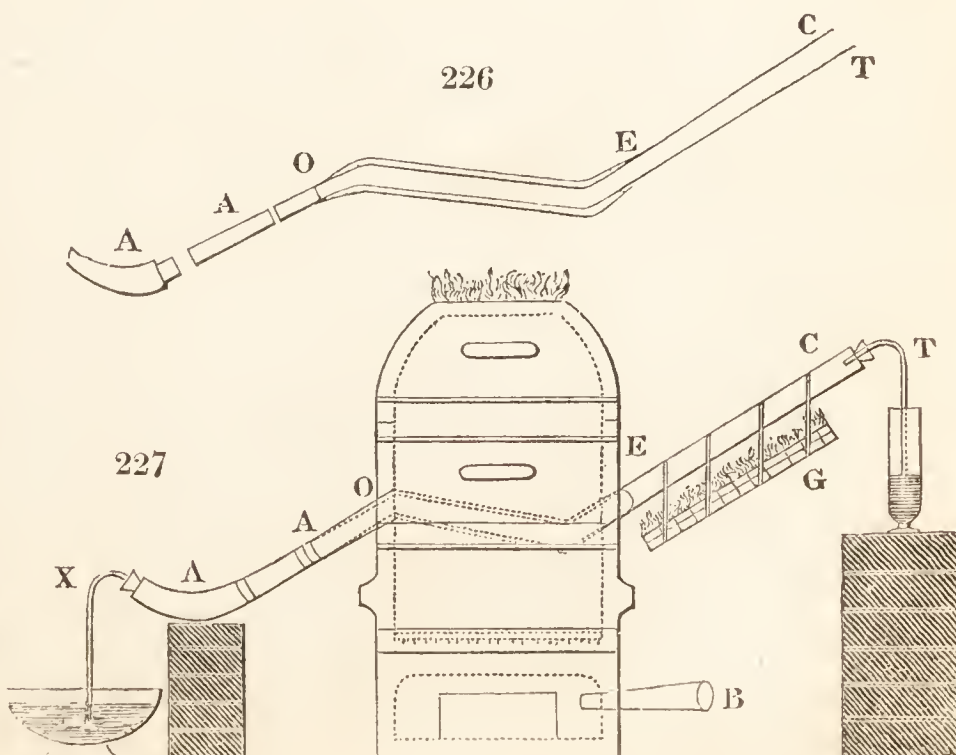
inquiry, and the latter involve numerous difficulties in consequence of the gradual transition of metals of one class into those of another. I shall consider the metals in the order in which they are set down in the following table, and which is nearly that of their respective attractions for oxygen, with the exception of the last division, which includes substances in part imperfectly examined, and from which, as already remarked, silicon ought probably to be excluded.

<p>I.</p> <p>1 Potassium 2 Sodium 3 Lithium 4 Calcium 5 Barium 6 Strontium 7 Magnesium</p>	<p>II.</p> <p>8 Manganese 9 Iron 10 Zinc 11 Tin 12 Cadmium 13 Cobalt 14 Nickel</p>	<p>III.</p> <p>15 Copper 16 Lead 17 Antimony 18 Bismuth 19 Uranium 20 Titanium 21 Cerium 22 Tellurium</p>
<p>IV.</p> <p>23 Arsenic 24 Molybdenum 25 Chromium 26 Vanadium 27 Tungsten 28 Columbium</p>	<p>V.</p> <p>29 Mercury 30 Silver 31 Gold 32 Platinum 33 Palladium 34 Rhodium 35 Osmium 36 Iridium</p>	<p>VI.</p> <p>37 Glucium 38 Zirconium 39 Yttrium 40 Thorium 41 Alumium 42 Silicium</p>

§ I. POTASSIUM.

POTASSIUM (or Kalium of the German chemists) was discovered in 1807 by Sir Humphry Davy (*Phil. Trans.*, 1808.) He obtained it by submitting hydrate of potassa, or caustic potash, to the decomposing action of Voltaic electricity: the metal was slowly evolved at the negative pole. By this process, however, it could only be procured in very minute quantities; and various other methods have been devised. The following is that described by Gay Lussac and Thenard (*Recherches Physico-chymiques.*)

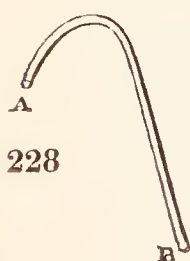
A sound and perfectly clean gun-barrel is bent, as shown in the annexed sketch (fig. 226). It is then covered with an infusible lute between the letters o and e, and the interior of the luted part is filled with clean iron-turnings. Pieces of fused potassa are then loosely placed in the barrel be-



tween E and C. A A is a copper tube and small receiver, which are adapted to the extremity o, and to each other, by grinding. This apparatus is next transferred to the furnace, arranged as shown in fig. 227, x and t representing two glass tubes dipping into mercury. The furnace is supplied with air by a good double bellows entering at B, and a small wire basket, G, is suspended below the space E C.

The part of the barrel in the furnace is now cautiously raised to a white heat, and the escape of air by the tube x shows that all is tight. Some burning charcoal is then put at the end E, of the cage G, which causes a portion of potassa to liquefy and fall into the low part of the barrel upon the iron. Hydrogen gas instantly escapes by the tube x, and attention must now be had to keep the copper tubes A A cool, by laying wet cloths upon them. When the evolution of gas ceases, fresh charcoal is placed under the potassa, and so on till the whole has passed down; if too much potassa be suffered to fall at once, the extrication of gas at x will be very violent, which should be avoided. If the space between A and o should become stopped by potassium, gas will issue by the tube t (which must always be under a greater pressure of quicksilver than the tube x,) and the potassium must be cautiously fused by applying hot charcoal to the copper tube, when the gas will again appear at x and cease at t. When the operation is concluded, the tubes x and t are removed, and corks quickly applied to the holes; and when the apparatus is cool, the barrel is carefully removed from the furnace, and a little naphtha suffered to run through it. The potassium is found in globules in the tube and receiver A A, and considerable portions often lodge at o. The success of this operation is certain, if the heat has been sufficient: but the barrel, if not very carefully covered with lute, is apt to melt, and much, if not the whole, of the product is lost.

Besides the above, there are other methods of obtaining potassium. M. Brunner (*Quarterly Journal*, xv. 379), employs a spheroidal wrought-iron bottle, of a capacity between a pint and a quart, and a piece of gun-barrel of the annexed shape is fitted to its neck by grinding at the end A. When this bottle is charged and well luted it is placed in a proper furnace, nearly perpendicularly, and so that the greater part of the tube may be exposed to heat (it being protected by coils of iron-wire rolled round it,) while the end B projects, and has attached to it a copper receiver with a small safety-tube. This receiver, when in use, is about half filled with naphtha, and kept cold by ice or cold water. The bottle is charged with four ounces of fused caustic potassa, introduced, in small portions, alternately, with 6 ounces of clean iron-turnings broken in a mortar, and 1 ounce of powdered charcoal; and this mixture is covered by 2 ounces more of iron-turnings: it is then placed in the furnace, and a glass tube inserted into the protruding barrel at B. As soon as the whole acquires a bright red-heat, inflammable gas is evolved, which burns with a violet flame, and shortly after the green vapour of potassium is seen in the glass tube, which is then removed, and the copper receiver substituted, so that the end B may dip into the naphtha. When the evolution of gas ceases, the fire is extinguished, and the receiver carefully removed. A very successful



result furnished 150 grains of potassium, in small globular masses. In another experiment the mixture in the retort consisted of 8 ounces of pure and fused carbonate of potassa, 6 of iron-turnings, finely bruised, and 2 of charcoal: from these, 140 grains of potassium were obtained. Calcined tartar was also sometimes employed instead of other forms of potassa.

The theory of these operations is by no means clearly understood in its minute details. When pure hydrate of potassa is employed in the gun-barrel experiment, more than a fourth of its weight of potassium is never obtained; the remainder is chiefly found partly undecomposed and partly in combination with the produced oxide of iron, forming a hard brittle compound, difficultly acted on by water. The evolution of potassium is evidently dependent upon the attraction of the iron at a high heat for oxygen; the water of the potassa is at the same time decomposed, and possibly the nascent hydrogen may perform its part in the reduction: the readiness with which potassium assumes the elastic state at high temperatures also contributes to its evolution; yet, when the exceedingly powerful attraction of potassium for oxygen is considered, the process is, as to its theory, obscure.

Obtained by the aid of charcoal, potassium generally contains a little carbon, which may be separated by redistilling it in a small iron or even glass retort, with its beak dipped into naphtha, but this is a troublesome process, and generally attended by some loss of the metal.

Wöhler has described a modification of the potassium apparatus, and a peculiar receiver for its condensation, contrived by Berzelius, of which a description will be found in the twenty-second volume of the *Quarterly Journal*, p. 206. He employs carbonate of potassa produced by calcining tartar, and uses charcoal as the reducing agent. In all these arrangements it is a point of importance to have the tubes, through which the metal passes into the naphtha, as short as possible, and of a sufficient diameter, otherwise they are apt to become plugged up\*.

Potassium is a white metal of great lustre. It instantly tarnishes by

\* During the distillation of potassium from a mixture of carbonate of potassa and charcoal, a gray compound distils over, which, by the action of water, yields a yellow solution, from which crystals may be obtained by evaporation: these consist of potassa in combination with a peculiar acid, which from the yellow colour of its salts has been called *croconic acid*. To obtain this acid the purified crystals of croconate of potassa are powdered and put into absolute alcohol, to which sulphuric acid (sp. gr. 1.78) is carefully added, so as barely to saturate the alkali. The yellow alcoholic solution is then poured off the precipitated sulphate of potassa, and the croconic acid obtained by evaporation. It is soluble in water, and yields prismatic crystals of a yellow colour, astringent

taste, and which redden litmus: it is not decomposed at a heat of 212°, but at high temperatures it deposits pure charcoal. Gmelin considers this acid as a compound of 5 atoms of carbon and 4 of oxygen, with apparently a small proportion of hydrogen, which, however, is less than 1 atom.

Anhydrous *croconate of potassa* is yellow and opaque: its crystals are orange-coloured prisms, transparent, inodorous, tasting like saltpetre; moderately soluble in cold, and very soluble in hot water, and insoluble in absolute alcohol: heated nearly to redness the salt suddenly glows throughout, rapidly evolving carbonic acid with a little carbonic oxide, and leaving a residue of carbonate of potassa and charcoal.

exposure to air, and is gradually converted into an oxide. At  $55^{\circ}$  it is malleable, and of the consistency of wax. Its specific gravity is about 0.865. It is most conveniently preserved in naphtha, either by immersing it in that liquid, or by dipping the pieces of metal into it, and keeping them thus varnished, in a small well-stopped phial. When used, the exterior must be wiped with blotting-paper, or scraped; or the naphtha may be driven off by a gentle heat. At  $150^{\circ}$  it enters into perfect fusion; and at a bright red heat, in close vessels, it boils, and rises in green vapour. At  $32^{\circ}$  it is a hard and brittle solid, of a crystallized texture. If heated in air, it burns with a brilliant purple flame. It is an excellent conductor of electricity and of heat, and its lustre is well shown by fusing it under naphtha upon a piece of crown-glass, to which it will adhere, and through which it is seen as brilliant as mercury.

**POTASSIUM AND OXYGEN.** The attraction of potassium for oxygen, under most circumstances, exceeds that of all other bodies; it is, consequently, the most powerful deoxidizing agent which we possess. It forms two definite compounds with oxygen, which we may call the *protoxide* and *peroxide*; Berzelius admits a *suboxide*, but it is probably a mixture of potassium with the protoxide. When potassium is thrown upon water it takes fire, hydrogen gas is evolved, and a solution of *protoxide of potassium*, or *potassa*, is formed. When plunged under water, the potassium decomposes it with explosive violence, but without ignition, and the volume of the hydrogen evolved may be assumed as the equivalent or indicator of the proportion of oxygen transferred to the metal; 100 parts of potassium are thus found to absorb 20 of oxygen; and if this be considered a protoxide, then  $20 : 100 :: 8 : 40$ ,—so that 40 will be the number representing potassium; and the *protoxide, in its dry or anhydrous state* ( $p + o$ ) or P, consists of

	Berzelius.	Davy.	Gay Lussac and Thenard.
Potassium 1 .. 40 .. 83.34 .. 83.05 .. 85 .. 83.371			
Oxygen 1 .. 8 .. 16.66 .. 16.95 .. 15 .. 16.629			
1	48	100.00	100.000

The equivalent of potassium, deduced from the analysis of the chloride of potassium by Berzelius, is 39.15; he also states that 100 of potassium combine with 20.412 of oxygen; so that upon these data, the equivalent of potassium would be between 39 and 40.

Potassa, in the state it is usually met with in laboratories, contains a considerable portion of water, as is rendered manifest by the action of iron at high temperatures; and there always remains in the gun-barrel, after the above-described experiment, a portion of *dry potassa* combined with oxide of iron. To obtain dry potassa, or *anhydrous protoxide of potassium* in its pure state, the metal may be exposed, at common temperatures, to the action of perfectly dry air or oxygen; or 1 part of potassium may be fused with 1.4 of the hydrated protoxide. It is a gray substance, fusible at a red heat, and volatile at a white heat. It combines very energetically with water to produce a *hydrate*, and what is commonly called caustic or pure potassa, is, in fact, this hydrate, composed of



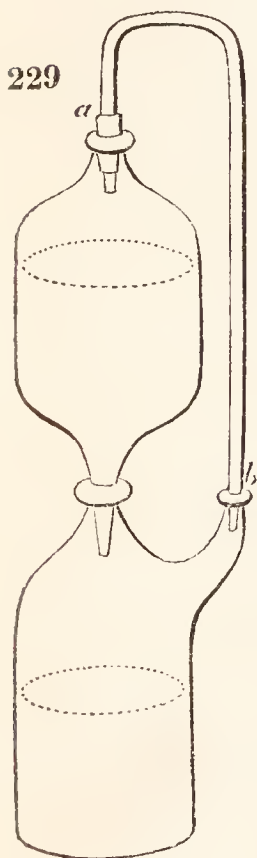
						Berzelius.
Potassa	1	..	48	..	84.2	.. 84
Water	1	..	9	..	15.8	.. 16
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>		<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	1		57		100.0	100

HYDRATED PROTOXIDE OF POTASSIUM, OR CAUSTIC POTASSA (P + Q), is procured in our laboratories by decomposing carbonate of potassa by lime. The best process consists in boiling in a clean iron vessel, pure carbonate of potassa, with half its weight of pure quick-lime, in water. The lime is gradually added to the boiling alkaline solution, which is kept constantly stirred, and towards the end of the operation it is tested, by filtering a small portion, and pouring it into three or four times its bulk of dilute nitric acid: if there be no effervescence, sufficient lime has been used; but if carbonic acid escapes, the ebullition with lime must be continued until the tested portion shows no signs of carbonic acid. The whole is then allowed to remain quiet, that the lime may subside; and the clear liquor or *ley* being poured off, is strained through clean linen, concentrated by evaporation, again strained, and set by in a well-stopped bottle till it admits of being decanted, perfectly clear from any sediment. The clear solution is to be evaporated to dryness, in a polished iron or pure silver basin. It is often cast into sticks for the use of surgeons, who employ it as a caustic, and in this state it generally contains some peroxide, and therefore evolves oxygen when dissolved in water. It is the *potassa fusa* of the *London Pharmacopœia*. It may be further purified by the action of alcohol, which dissolves the pure hydrate, and leaves earthy and other impurities: the alcohol is then driven off by heat. In this case the alcohol is always, in some measure, acted upon by the potassa, and a portion of carbonaceous matter deposited, so that it should be allowed to remain as short a time as possible combined with the alkali. Having obtained the dry caustic alkali by lime, it may be boiled in a silver basin with highly-rectified alcohol for a few minutes, and then set by in a stopped phial; when the impurities are deposited, the alcoholic solution may be poured off and rapidly evaporated to dryness in a silver basin; or if the quantity of alcohol be considerable, it may be distilled off in a silver alembic with a glass head: the heat may then be raised so as to fuse the potassa, which, on cooling, should be broken up and preserved in well-closed phials.

HYDRATE OF POTASSA, thus purified, is white, very acrid and corrosive, and at a bright-red heat evaporates in the form of white acrid smoke. At a white heat it is decomposed by charcoal, and carburetted hydrogen, carbonic oxide, and potassium are formed. It quickly absorbs moisture and carbonic acid from the air, and at 60° one part of water dissolves two. It may be crystallized in octoëdrons, by keeping a strong aqueous solution of it for some time in a stopped phial. The crystals contain much water of crystallization, but the exact quantity has not been ascertained. It is highly alkaline, powerfully reddening turmeric, and converting several vegetable blues to green: it also acts energetically upon the greater number of organic products, and unites with the fat oils to form soap, hence the term *soap-lye*. Being exclusively procured from vegetables; it was formerly called *vegetable alkali*; but it also exists in

certain minerals\*, and in a few animal secretions. When touched with moist fingers it has a soapy feel, in consequence of its action upon the cuticle. In the fused state it produces heat when dissolved in water; but in its crystallized state it excites considerable cold, especially when mixed with snow. At a natural temperature of  $30^{\circ}$ , M. Lowitz found that equal weights of crystallized potassa and snow depressed the thermometer  $45^{\circ}$ . (*Ann. de Chim.*, xxii.) It dissolves sulphur and several sulphurets, and alumina and silica. The oxides of manganese, zinc, tin, lead, antimony, cobalt, arsenic, molybdenum, tungsten, and nickel, are also soluble in aqueous solution of potassa.

THE LIQUOR POTASSÆ OF THE PHARMACOPŒIA is directed to be prepared as follows:—"Take of subcarbonate (carbonate) of potassa a pound; fresh lime, half a pound; boiling distilled water, a gallon. Dissolve the subcarbonate in two pints of the water; add the remaining water to the lime; mix the hot liquors together; then set the mixture by in a covered vessel, and after it has cooled, filter the solution through a cotton strainer. If effervescence be excited by dropping any diluted acid into the solution, more lime must be added, and the solution again strained. A pint of this solution ought to weigh 16 ounces troy." Its specific gravity in that case is 1.056 †.



Whilst the solution of potassa is filtering, it is apt to absorb a little carbonic acid from the air, which may be prevented, upon the small scale, by covering the funnel with a plate of glass, and receiving it into a bottle as nearly air-tight as possible; or the annexed filtering-apparatus, fig. 229, contrived by Mr. Donovan (*Annals of Philosophy*, xxvi., 115,) may be used. It consists of two glass vessels connected by a tube, made air-tight by perforated corks at the junctions *a* and *b*. The upper vessel terminates in a conical pipe, ground into the lower one, and into which is stuffed a piece of coarse linen.

In all cases where solutions of potassa are employed, it must be recollected that they gradually act upon glass, especially upon common white glass; hence green glass vessels are preferable: but where alkaline solutions are to be exposed to heat, even these communicate some impurity, and in such cases vessels of pure silver can only be relied upon.

\* Fuchs says that it may be economically obtained from certain varieties of felspar: for this purpose they are calcined with lime, then left for some time in contact with water, and the liquor filtered and evaporated. He says he has thus procured 19 per cent. from felspar and 15 from mica.

† The solution of caustic potassa is frequently impure from the presence of carbonic acid, silica, alumina, lime, and sulphuric or muriatic acid. If nitric

acid cause an effervescence when dropped into it, it indicates *carbonic acid*; if a gelatinous precipitate, not soluble in very slight excess of acid, it is *silica*; if soluble, it is *alumina*. The presence of *lime* is shown by adding oxalate of ammonia to the solution previously neutralized by nitric acid: in the same solution, nitrate of silver will indicate muriatic acid or *chlorine*, and nitrate of baryta, *sulphuric acid*.

It may sometimes be useful to know the quantity of real potassa contained in watery solutions of different specific gravities; the following are the results of Mr. Dalton's experiments, in reference to this question:—

Specific Gravity.	Potassa per Cent.	Boiling Point.	Specific Gravity,	Potassa per Cent.	Boiling Point.
1.68	51.2	329°	1.33	26.3	229°
1.60	46.7	290	1.28	23.4	224
1.52	42.9	276	1.23	19.5	220
1.47	39.6	265	1.19	16.2	218
1.44	36.8	255	1.15	13.	215
1.42	34.4	246	1.11	9.5	214
1.39	32.4	240	1.06	4.7	213
1.36	29.4	234			

PEROXIDE OF POTASSIUM. ( $p + 3O$ .) When potassium is burned in a silver spoon in oxygen gas, a yellow fusible substance is obtained, which, on cooling, acquires a scaly crystalline appearance. It consists, according to Gay Lussac and Thenard, of

					Gay Lussac and Thenard.
Potassium	1	...	40	...	62.4
Oxygen	3	...	24	...	37.6
	<u>1</u>		<u>64</u>		<u>100.0</u>
					65
					35
					<u>100</u>

This substance has some singular properties; it supports the combustion of most of the inflammables, and when heated in hydrogen gas, diminishes its bulk and forms water: it decomposes ammonia under the same circumstances. When put into water, a copious effervescence ensues, arising from the escape of oxygen gas, and a solution of potassa is obtained. When hydrate of potassa is fused in an open crucible, a portion of its water is disengaged, and oxygen absorbed, so as to form this peroxide; and hence it is, that common caustic potassa almost always effervesces, and gives out oxygen upon the affusion of water. When potassium is dropped into melted nitre, the peroxide is also formed; likewise by passing oxygen over potassa heated to redness.

POTASSIUM AND CHLORINE act very energetically on each other, the metal taking fire and burning brilliantly in the gas, especially if introduced into it in the state of fusion, as, otherwise, a crust of chloride is apt to form upon it and protect the interior from further action. They produce the white compound which has been called *muriate of potash*, but which is a true *chloride of potassium* ( $PO + C$ ) consisting of

					Ure.
Potassium	1	...	40	...	52.6
Chlorine	1	...	36	...	47.4
	<u>1</u>		<u>76</u>		<u>100.0</u>
					53
					47
					<u>100</u>

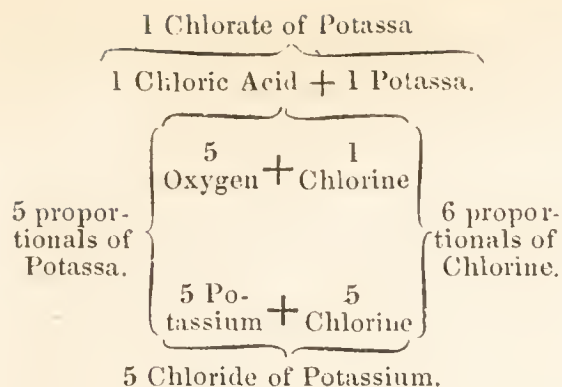
When potassium is heated in gaseous muriatic acid, this compound is formed, and hydrogen is evolved; an experiment already adverted to under the article *Muriatic Acid* (p. 361.) It is also formed by dissolving potassa or its carbonate in muriatic acid, and evaporating to dryness. It dissolves in three parts of water at 60°, or, according to Gay Lussac, 100

parts of water at  $32^{\circ}$  dissolve 29.23, and for every  $1.8^{\circ}$  above 32, the water takes up 0.2738 more of the salt. One part of the powdered salt stirred into four parts of cold water produces a depression of temperature of between  $20$  and  $25^{\circ}$ , whereas common salt under the same circumstances only depresses the thermometer between  $2^{\circ}$  or  $3^{\circ}$ . It crystallizes in cubes, which are anhydrous; its taste is saline and bitter. In old pharmacy it was called *digestive salt of Sylvius*; also, *regenerated sea-salt*. It is soluble in alcohol. When intensely heated in open vessels, it evaporates in the form of white smoke. This salt is a residue of several chemical and pharmaceutical processes, and is sometimes found in considerable quantities in rough salt-petre, where it is often mistaken for common salt: the manufacturers of alum occasionally employ it as the source of potassa in that salt.

CHLORATE OF POTASSA  $(p + o) + (c + 5o)$  or  $(P + chl')$  is formed by passing chlorine through a solution of potassa. Chloride of potassium is one of the results, the other is *chlorate of potassa*, a salt in brilliant rhomboidal tables (formerly called *oxymuriate of potash*). Its crystalline forms have been described by Mr. Levy (*Quarterly Journal*, xv. 286), and by Mr. Brooke (*Ann. Phil.*, v. 451).

This salt is prepared, upon the large scale, by charging one or two Woulfe's bottles with solution of carbonate of potassa, and passing chlorine slowly through it, at the lowest convenient temperature: the gas is absorbed, and the liquor effervesces, chiefly from the escape of carbonic acid; when this has ceased, the liquor may be put aside in a cold dark place for about 24 hours, when it will be found to have deposited a considerable portion of the crystallized chlorate, which may be taken out, drained, and purified by solution in hot water, which, during cooling, again deposits the salt in white crystalline scales. The mother-liquor, from which more of the salt may be obtained by evaporation, is generally of a pinkish tint, from the presence of a trace of manganese; but this tint disappears when sufficiency of chlorine has been passed in to saturate it, and it acquires a brownish hue\*. Solution of pure potassa absorbs the gas more readily than the carbonate, but nearly with the same phenomena, and in either case care must be taken that the tube conveying the chlorine does not become stopped up by the salt, which is apt to happen if it be not sufficiently capacious. To understand the theory of this process we must recollect that chloric acid is a compound of one proportional of chlorine and five of oxygen, and that chloride of potassium consists of one proportional of chlorine and one of potassium, and that potassa contains one proportional of oxygen and one of potassium: it follows, then, that five proportionals of chlorine acting upon five of potassa will expel five of oxygen, which, uniting with one of chlorine, will form one proportional of chloric acid, and this uniting to a proportional of the undecomposed potassa will form chlorate of potassa, as shown in the following diagram:—

\* In this process, the carbonic acid is expelled when excess of chlorine is passed into the solution: by particular management chlorine may be retained in a solution of carbonated alkali, forming a very peculiar compound. See *Carbonate of Soda*.



It appears, therefore, that five proportionals of potassa will require six of chlorine to be consumed in the formation of five proportionals of chloride of potassium, and one proportional of chloric acid. The elements of the water are not concerned in the formation of these products, but that fluid performs the important office of enabling the different elements to act upon each other in their nascent states.

The taste of this salt is cooling and austere. When pure, its aqueous solution is not rendered turbid by nitrate of silver. When triturated, it appears phosphorescent. It is anhydrous. When exposed to a dull-red heat it decrepitates, fuses, gives out nearly 40 per cent. of its weight of oxygen, and chloride of potassium remains. It is soluble in 18 parts of cold and 2.5 of boiling water; or, according to Gay Lussac, 100 parts of water at 32° dissolve 3.5 parts, at 59° 6 parts, at 95° 12 parts, at 120° 19 parts, and at 216°, which is the boiling-point of the saturated solution, 60 parts. It acts very energetically upon many inflammables, and triturated with sulphur, phosphorus, and charcoal, produces inflammation and explosion. A mixture of three parts of this chlorate with one of sulphur, detonates loudly when struck upon an anvil with a hammer, and even sometimes explodes spontaneously; hence it should not be kept ready mixed. Chlorate of potassa was proposed by Berthollet as a substitute for nitre in gunpowder. The attempt was made at Essone in 1788: but, as might have been expected, no sooner was the mixture of the chlorate with the sulphur and charcoal submitted to trituration, than it exploded with violence, and proved fatal to several people. With phosphorus the detonation is dangerously violent. The experiment is best made, by wrapping a grain of phosphorus and two of the chlorate in a small piece of paper, and striking them a blow with a hammer, upon an anvil. The phosphorus is generally thrown about in an inflamed state. These phenomena depend upon the decomposition of the chloric acid.

The action of sulphuric acid upon chlorate of potassa has already been adverted to. (See *Oxides of Chlorine*, p. 337.) If, instead of distilling the yellow mixture of the acid and chlorate with the caution there described, it be heated to about 150°, it suddenly explodes. The theory of the production of chloric oxide is more explicitly described in the next article.

When sulphuric acid is dropped upon mixtures of this salt and combustibles, instant ignition ensues in consequence of the evolution of oxide of chlorine. A mixture of sugar and the chlorate thus treated, is immediately kindled, with a red and blue flame; and a mixture of sulphuret of antimony and the salt, suddenly deflagrates with a bright puff of flame and smoke: the latter mixture requires to be cautiously made, as it often takes fire by mere trituration. Matches tipped with some of these inflammable mixtures, and called *Lucifers*, are now in common use, and are inflamed either by friction or by the contact of sulphuric acid, which is most conveniently applied by putting some asbestos into a small well-

stopped phial, and moistening it with sulphuric acid; the match is rapidly dipped into the phial and inflames on touching the asbestos, without the risk of spiriting about the acid. Some of the matches which inflame by a pinch or blow, contain a portion of a drop of sulphuric acid hermetically sealed in a piece of very small and thin glass tube, and which escapes when broken, and acts upon the inflammable mixture. Berzelius gives the following as the best composition for the match: 30 parts of powdered chlorate of potassa, 10 of powdered sulphur, 8 of sugar, 5 of gum-arabic, and a little cinnabar. The sugar, gum, and salt, are first rubbed together into a paste with a sufficiency of water; the sulphur is then added, and the whole being thoroughly beaten together, small brimstone matches are dipped in, so as to retain a thin coat of the mixture upon their sulphuretted points: they should be quite dry before they are used. One of the compounds occasionally employed in percussion gun-locks is a similar composition: 10 parts of gunpowder are rubbed with water, and the soluble part poured off; the remaining paste is then mixed with  $5\frac{1}{4}$  parts of finely-powdered chlorate of potassa, and a drop of it put into each of the small copper caps adapted to the peculiar tubular touch-hole of the gun; a blow being struck upon the cap the powder is inflamed, and communicates to that in the barrel. The great disadvantage of this compound is, that it forms products which soon rust the touch-hole and surrounding parts: fulminating mercury is, therefore, now generally substituted.

When sulphuric or nitric acids are poured upon mixtures of chlorate of potassa and certain combustibles under water, by means of a long funnel, inflammation also ensues. In this way a beautiful experiment may be made with phosphorus, a few small pieces of which are put at the bottom of a tall glass of water, and a little of the chlorate thrown in upon it; sulphuric acid is then carefully introduced into the contact of the salt by a funnel, with a tube long enough to reach it; the phosphorus presently inflames and burns vividly in different parts of the fluid, forming a kind of well of fire. A few grains of this salt put into a teaspoonful of muriatic acid, and then diluted with water, form an extemporaneous bleaching-liquor.

The ultimate elements of chlorate of potassa are

Oxygen	..	6	..	48	..	38.70
Chlorine	..	1	..	36	..	29.05
Potassium	..	1	..	40	..	32.25
		<hr/>		<hr/>		<hr/>
		1		124		100.00

Or it consists of

Potassa	.	1	..	48	..	38.70	..	Berzelius.
Chloric acid	.	1	..	76	..	61.30	..	61.51
		<hr/>		<hr/>		<hr/>		<hr/>
		1		124		100.00		100.00

OXYCHLORATE OR PERCHLORATE OF POTASSA  $(p + o) + (c + 7o)$  or  $(P + C'')$  may be formed by moistening one part of chlorate of potassa with three of sulphuric acid, and subsequently carefully warming the mass till it becomes white, and the oxide of chlorine is expelled: in this state it consists of bisulphate and oxychlorate of potassa, which may be sepa-

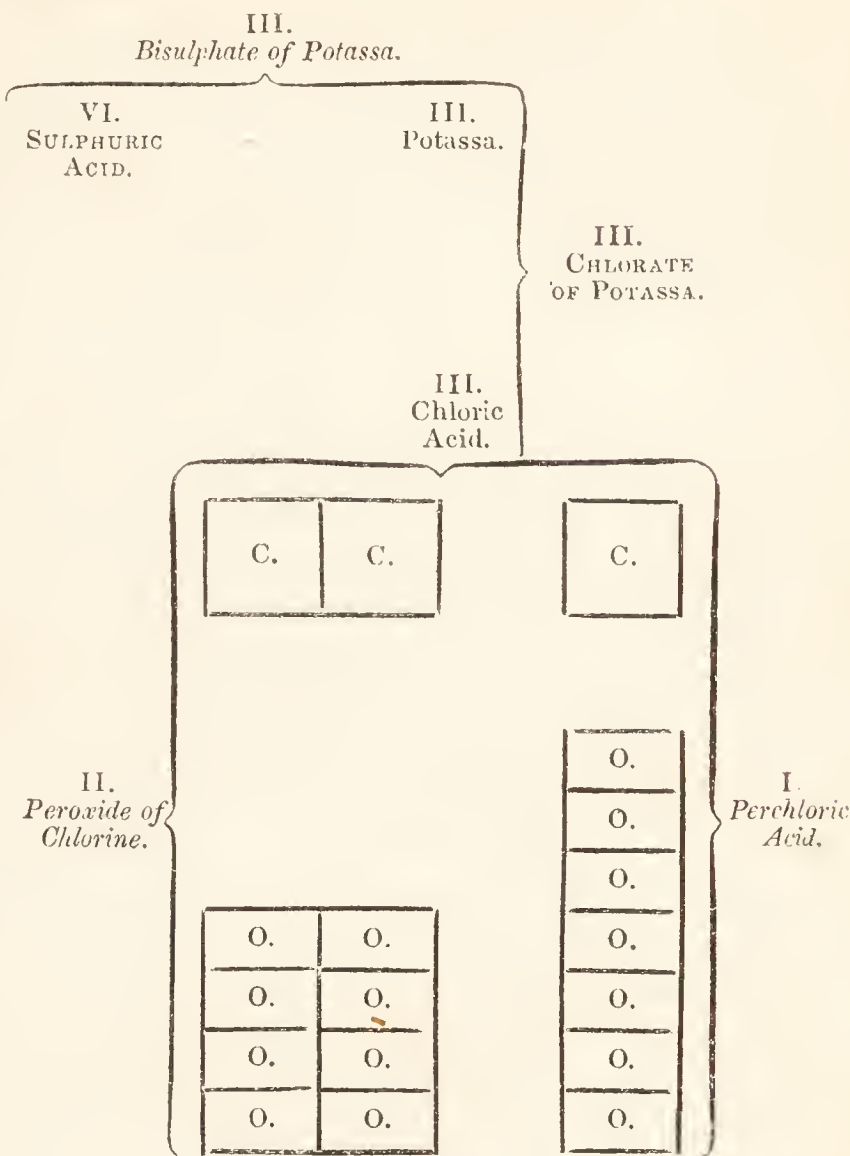
rated by solution and crystallization, the former being much more soluble in cold water than the latter salt.

In reference to the production of peroxide of chlorine and perchloric acid, as the result of the action of sulphuric acid upon chlorate of potassa, the annexed diagram may, perhaps, be useful. The original substances are printed in capitals, the components in common type, and the resulting compounds in italics; the volumes of oxygen and of chlorine being shown by the usual symbols of bulks which I have elsewhere employed. The Roman numerals denote the number of proportionals presumed to be employed.

Thus it appears that six proportionals of sulphuric acid acting upon three of chlorate of potassa form three of bisulphate of potassa, and detach three of chloric acid, the elements of which are three of chlorine and fifteen of oxygen: of these, two of chlorine and eight of oxygen form two of peroxide of chlorine; and the remaining one of chlorine and seven of oxygen form perchloric acid. If instead, as in the above diagram, of considering the mere formation of perchloric acid, we refer to the formation of perchlorate of potassa, we must assume that the oxygen is transferred to the chloric acid of an undecomposed portion of chlorate of potassa, and so converts it into perchlorate.

Oxychlorate of potassa does not change vegetable colours, nor is it altered by exposure to air. It crystallizes in octoëdra. It requires rather more than 50 parts of water at 60° for its solution: but is much more soluble in boiling water. It is insoluble in alcohol: it detonates slightly when rubbed with sulphur. When mixed with its own weight of sulphuric acid, and distilled at 280°, solution of oxychloric acid passes over. It may be decomposed by exposure to a temperature of 412°. Oxygen is given off, equal to 0.45 per cent. of the weight of the salt, and chloride of potassium remains in the retort.

Gmelin states that when a saturated solution of chlorate of potassa is exposed to the decomposing agency of Voltaic electricity, transmitted by platinum poles, crystals of oxychlorate of potassa are formed at the positive pole, whilst hydrogen is evolved at the negative.



This salt consists of

Oxygen	..	8	..	64	..	45.7
Chlorine	..	1	..	36	..	25.7
Potassium	..	1	..	40	..	28.6
		<hr/>		<hr/>		<hr/>
		1		140		100.0

Or,

Potassa	.	1	..	48	..	34.3	..	Stadiou.	34.31
Chloric acid	.	1	..	92	..	65.7	..		65.69
		<hr/>		<hr/>		<hr/>			<hr/>
		1		140		100.0			100.00

IODIDE OF POTASSIUM. (*po + i.*) Iodine and potassium act upon each other very energetically, evolving heat and light, and a crystalline compound is obtained, white and fusible. When hydriodic acid is saturated by potassa, and the solution carefully evaporated, anhydrous prismatic crystals of the iodide (or as it is usually called in medicine, *hydriodate of potassa*) are obtained. The readiest mode of procuring this compound consists in dissolving iodine in solution of potassa, till it begins to assume a brown colour: on evaporating to dryness, and fusing the residuary salt, a pure iodide of potassium remains. If, instead of fusing the products, the solution be carefully evaporated nearly to dryness, and alcohol poured upon it, the iodide is dissolved, and there remains a salt insoluble in alcohol, which is iodate of potassa, and which, at a red heat, evolves oxygen, and becomes iodide of potassium. The action of iodine upon the alkali appears in all respects to correspond with that of chlorine. Iodide of potassium is also frequently prepared by decomposing a solution of iodide of zinc by carbonate of potassa, and filtering off and evaporating the resulting solution of the iodide. It forms cubic and octoëdral crystals, which are deliquescent. According to Gay Lussac, 100 parts of water at 65° dissolve 143 of this salt: it is sparingly soluble in absolute alcohol, but much more so in alcohol, sp. gr. 850. It is pretty largely used in medicine, and as it occurs in commerce is frequently mixed with chloride of potassium and sodium, and with sulphate or carbonate of potassa. It should be purchased in crystals, which ought not to be very deliquescent, and should perfectly dissolve in alcohol.

Iodide of potassium consists of

Potassium	..	1	..	40	..	24.2	..	Gay Lussac.	23.8
Iodine	..	1	..	125	..	75.8	..		76.2
		<hr/>		<hr/>		<hr/>			<hr/>
		1		165		100.0			100.0

The aqueous solution of iodide of potassium dissolves a considerable portion of iodine; this solution, under the name of *ioduretted iodide of potassium*, is sometimes used in medicine: it is of a deep-brown colour.

IODATE OF POTASSA, (*p + o*) + (*i + 5o*) or *P + i'*, obtained as just described, is a white, difficultly soluble salt, requiring about 14 parts of water at 60° for its solution: at a red heat, it gives out between 22 and 23 per cent. of oxygen, and is converted into iodide of potassium. Iodide of potassium may also be converted into iodate of potassa, by fusing it



in a crucible, and projecting upon it rather less than twice its weight of chlorate of potassa: warm water removes the chloride of potassium and leaves the iodate.

This salt is insoluble in alcohol: it forms small and permanent prismatic crystals, soluble without decomposition in warm sulphuric acid, and detonating with a purple flame when thrown upon hot coals. With the addition of potassa, it yields a crystallizable subsalt, the exact composition of which has not been determined; it is very soluble. Iodate of potassa consists of

Potassa	.	1	..	48	..	22.55
Iodic acid	.	1	..	165	..	77.45
		1		213		100.00

Serullas has described a biniodate and a teriodate of potassa. (*Ann. de Chim. et Phys.*, XLiii., 113.)

**BROMIDE OF POTASSIUM.** ( $po + b.$ ) Potassium and bromine act intensely upon each other, evolving heat and light, and producing explosion. When bromine is dropped into solution of potassa, and the mixture evaporated to dryness, a *bromide of potassium* is also obtained: it is white, fusible, and crystallizes in cubes, easily soluble in water, and slightly so in alcohol. It consists of

Potassium	..	1	..	40	..	33.9
Bromine	..	1	..	78	..	66.1
		1		118		100.0

It is prepared for medical use, either by the above process, or by decomposing bromide of zinc by carbonate of potassa, and should be purchased in crystals, as it is otherwise apt to be impure.

When ethereal solution of bromine is agitated with liquid potassa, the yellow colour disappears, and bromate of potassa and bromide of potassium are the results. The action, therefore, of bromine, is here analogous to that of chlorine and iodine.

**BROMATE OF POTASSA** ( $po + o$ ) + ( $b + 5o$ ) or ( $P + b'$ ) separates in the form of a crystalline powder, when bromine and solution of potassa are mixed in sufficient quantities. It scintillates on a hot coal, like nitre, and evolving oxygen, becomes bromide of potassium. It is slightly soluble in alcohol, readily soluble in water, and crystallizes in needles: mixed with sulphur, it detonates by a blow. Its solution occasions a white precipitate in nitrate of silver. (Balard, *Quarterly Journal*, xxii. 389.)

**POTASSIUM AND FLUORINE.** When hydrofluoric acid is saturated with potassa, and evaporated to dryness, a deliquescent and very difficultly crystallizable compound is obtained, which must be regarded as a *fluoride of potassium*. ( $po + f.$ ) It probably consists of

Potassium	.	1	..	40	..	71.5
Fluorine	.	1	..	18	..	28.5
		1		58		100.0

This fluoride bears an intense heat without change.

Berzelius has described an apparently peculiar compound, obtained by dissolving the above fluoride in hydrofluoric acid, and evaporating to

dryness in a platinum vessel: it is crystallizable, readily soluble in water, and when heated to incipient redness is decomposed, hydrofluoric acid being evolved, and fluoride of potassium remaining. It appears to consist of

					Berzelius.			
Fluoride of Potassium	.	1	. . .	58	. . .	75.3	. . .	74.9
Hydrofluoric acid	.	.	. . .	19	. . .	24.7	. . .	25.1
		<hr style="width: 100%;"/>		1		<hr style="width: 100%;"/>		<hr style="width: 100%;"/>
				77		100.0		100.0

**POTASSIUM AND HYDROGEN.** When potassium is heated in hydrogen, it absorbs a portion of the gas, and produces a gray infusible *hydruret*, destitute of lustre, and burning vividly when heated in air or oxygen gas. When heated, *per se*, it evolves hydrogen; and the same change takes place in the contact of mercury. When hydrogen and potassium are passed together through a white-hot tube, the gas dissolves the metal, and produces a spontaneously inflammable *potassiuretted hydrogen gas*. Potassiuretted hydrogen is also produced when potassium is thrown upon water, and is the cause of the red flame and white fumes produced during its combustion under such circumstances. Both these compounds are usually formed during the operation for obtaining potassium by the gun-barrel.

**NITRATE OF POTASSA; NITRE; SALTPETRE.**  $(po + o) + (n + 5o)$  or  $(P + n')$  This salt is an abundant natural product, and is principally brought to this country from the East Indies, where it is produced by lixiviation from certain soils.

The greater part of the rough nitre imported from the East Indies is in broken crystals of a brown colour, and more or less deliquescent; exclusive of other impurities, it often contains a very considerable proportion of common salt, which, re-acting upon the nitre, induces the production of a portion of nitrate of soda and chloride of potassium. It also usually contains sulphate of lime, and often evident traces of organic matter.

In Germany and France it is artificially produced in what are termed nitre-beds. Thenard (*Traité de Chimie Elémentaire*, tom. ii., p. 511) has described the French process at length. It consists in lixiviating old plaster rubbish, which, when rich in nitre, affords about five per cent. Refuse animal and vegetable matter, which has putrefied in contact with calcareous soils, produces nitrate of lime, which affords nitre by mixture with sub-carbonate of potassa. In the same way it is abundantly produced in some parts of Spain. Exudations, containing saltpetre, are not uncommon upon new walls, where it appears to arise from the decomposition of animal matter contained in the mortar. It was long ago shown by Glauber, that a vault plastered over with a mixture of lime, wood-ashes, and cows' dung, soon becomes covered with efflorescent nitre, and that, after some months, the materials yield, on lixiviation, a considerable proportion of that salt.

The loss which rough nitre sustains in refining, is technically termed the *refraction*, and can only be ascertained by analysis, which frequently is somewhat difficult and intricate: it is, moreover, not easy to get a fair sample of a cargo. The samples which the merchants and brokers select

for analysis, generally consist of portions drawn from each bag and afterwards mixed together, and if carelessly or unfairly taken, or exposed so as to become more moist or more dry than the bulk, the report of the analyst is often unsatisfactory. He should work upon not less than 25 to 50 lbs. of such sample, which should be ground or triturated so as to produce a properly uniform mixture of the whole, for it often includes lumps of pure nitre or of common salt; of this uniform mixture a portion is then taken for analysis. The moisture is determined by the loss occasioned by drying a given weight on the sand-bath. A portion is then dissolved in water and tested, so as to acquire some general notion of the impurities; and, from the effect of nitrate of silver, nitrate of baryta, and oxalate of ammonia, the presence of chlorides, sulphuric acid, and lime, is determined: the lime is generally in the state of sulphate, and more or less sulphate of potassa is also usually present; the chlorine is chiefly derived from the chlorides of potassium and sodium. Another portion of the sample should be dissolved in about thrice its weight of boiling water, and filtered, by which the sand and other insoluble impurities are collected; the salt should then be crystallized in the usual way, during which, the appearances and forms of the successive deposits will indicate, to the experienced eye, the nature of the foreign salts present; among which nitrate of soda, sulphate of potassa, sulphate and nitrate of lime, and chloride of sodium and potassium, with traces of chloride of calcium, and sometimes of a peculiar organic matter, are frequently found. It will be obvious that the accurate quantitative analysis of such a mixture of salts is not a very easy problem, and yet, the separation of nitrate of soda from nitrate of potassa, and of chloride of potassium from chloride of sodium, are essential steps, inasmuch as the value of the sample is materially affected by their relative proportions; for nitrate of soda, to say nothing of its unfitness for the manufacture of gunpowder, is cheaper than nitrate of potassa; and chloride of sodium is of no value, whilst chloride of potassium is purchased by the alum-makers; so that a sample of nitre, containing the latter salt, is in this respect worth more than where it only contains common salt. But inasmuch as the equivalent of chloride of sodium is only 60, and that of chloride of potassium 76, it is obvious that if the whole of the chlorine, as indicated by the weight of the chloride of silver, be considered as in combination with sodium (part of the sample consisting of chloride of potassium), the refraction will be estimated below the mark. Hence the necessity of ascertaining the relative proportions of both chlorides, which can only be effected by converting them into sulphates, and separating them by crystallization. When the common process for refining nitre is conducted as follows, it may be made subservient to the more accurate analysis.

**PURIFICATION OF NITRE.** A given quantity of the rough salt (say 7 lbs.) is accurately weighed, and then dissolved by heat in three or four parts of water; when boiling, the scum is removed until no more rises, and then the solution is allowed to settle for ten minutes or longer. In this way nearly all the dirt falls down, and the clear solution, being poured off, is passed through a filter of tow into a pan, and set aside to crystallize; the dirt left behind is added to the scum, and both being diluted, are filtered through paper, and the clear solution preserved. Next day the crystals

formed in the pan are separated and put into funnels to drain, and the mother-liquor with the filtered solution from the scum, &c., are further evaporated, and again left to crystallize. On the second evaporation, impurities generally separate from the solution; these are sometimes oxide of iron, or sulphate of lime, but most frequently chloride of sodium and of potassium, sulphate of potassa, and nitrate of soda. The two first are easily separated by filtration; the chlorides are best separated by evaporating the solution considerably, until much salt has been deposited, and then pouring the whole upon a filter of tow; the common salt, with more or less of the others, will remain on it, and should be washed by water to separate the nitre, which water should be added to the liquor, and the whole then brought to the crystallizing point. When cold, the crystals deposited by this solution are to be separated as before, until the mother-liquor is divided into other salts and nitre. It frequently happens that the crystals from the two or three last evaporations are coloured or contaminated by the adhesion of common salt, sulphate of lime, &c.; in this case, they should be re-dissolved and re-crystallized with the same precautions as before. Care should be taken in drying the crystals, especially when large, that no water remain in the interstices or cleavages between them, which is often the case to a considerable extent; and not unfrequently the interstitial water retains foreign salts, so that, in purifying nitre upon the large scale, it is often advantageous to stir it whilst crystallizing, that the crystals may be small and broken, and then the adhering impurities may be better washed out by cold water. When pure, the solution of nitre is not rendered turbid either by nitrate of silver or nitrate of baryta.

Nitre crystallizes in six-sided prisms, usually terminated by dièdral summits. Its primitive form is a right rhombic prism, the measurement and modifications of which have been given by Mr. Levy (*Quarterly Journal*, xv., 284.) The crystals are large and smooth when obtained from a great mass of solution, but irregular and striated when formed in smaller quantities. The large crystals are very sensible to changes of temperature, and when handled, generally crack transversely; so that it is difficult to preserve them entire. They are not altered by exposure to air. According to Bergman, nitre dissolves in 7 parts of water at  $60^{\circ}$ , and in its own weight at  $212^{\circ}$ ; but these proportions are not correct: La Grange states that 1 part of nitre dissolves in between 3 and 4 of water at  $60^{\circ}$ , and in half its weight at  $212^{\circ}$ . Gay Lussac has shown that the solubility of nitre varies extremely with temperature: at  $32^{\circ}$ , 100 parts of water dissolve 13.2 of the salt; at  $77^{\circ}$ , the salt dissolved by 100 of water is 38 parts; at  $132^{\circ}$ , it amounts to 97 parts; at  $176^{\circ}$ , to 169 parts; at  $210^{\circ}$ , to 236 parts; and at  $212^{\circ}$  to 246 parts. According to Dr. Ure, the temperature of a saturated solution of nitre, boiling hot, is  $340^{\circ}$ , and the relation of the salt to its solvent is in weight as 3 to 1. Upon the same authority, water at  $60^{\circ}$  dissolves one-fourth its weight of nitre; or, more exactly, this saturated solution contains 21 per cent. of salt: its specific gravity is 1.1415; and 100 parts in volume of the two constituents occupy now 97.91 parts. (*Jour. Royal Inst.*, i. 121.) Berzelius observes, that the solubility of nitre is apparently increased by the presence of common salt, but that this arises from their mutual

reaction, producing nitrate of soda and chloride of potassium. During the solution of 1 part of powdered nitre in 5 of water, the temperature sinks from  $50^{\circ}$  to  $35^{\circ}$ . Its use in cooling mixtures has already been noticed, p. 155. It is insoluble in pure alcohol. The crystals of nitre, though the salt is anhydrous, always contain interstitial water; so that they appear moist when powdered, and lose weight on drying. The taste of nitre is cooling and peculiar, and it is used in medicine in small doses, as a diuretic and sedative: in doses of from half an ounce to an ounce it is eminently poisonous, exciting violent spasms, vomiting, bloody stools, convulsions, and generally proving fatal. In such cases, viscid mucilaginous drinks with opium and cordials are the most effective restoratives. This salt consists of

						Wollaston.
Potassa	1	..	48	..	47.1	.. 46.668
Nitric acid	1	..	54	..	52.9	.. 53.332
	1		102		100.0	100.000

Its ultimate components are,

Oxygen	6	..	48	..	47.10
Nitrogen	1	..	14	..	13.75
Potassium	1	..	40	..	39.15
	1		102		100.00

At a temperature of about  $600^{\circ}$ , nitre fuses without undergoing change of composition, and congeals, on cooling, into a white striated mass. Sometimes it is cast into small balls or cakes, called *sal prunella*, a name derived from the circumstance of its having been occasionally stained of a plum-colour. At a red heat, nitre is slowly decomposed; and if distilled in an earthen retort or gun-barrel, it affords abundance of oxygen gas, one pound yielding about 12,000 cubic inches, of sufficient purity for many common experiments in which that gas is used; it is of course mixed with a portion of nitrogen. In this decomposition the nitre is first converted into *hyponitrite of potassa*, which is deliquescent; and afterwards, according to Berzelius, compounds are formed of potassa with nitric and nitrous oxides.

Nitre is rapidly decomposed by charcoal at a red heat; and the results are carbonic oxide and acid, nitrogen, and subcarbonate of potassa, formerly called *nitrum fixum*, and *white flux*. The old chemists used to perform this detonation in retorts connected with capacious receivers, which were generally blown to pieces; sometimes they succeeded in obtaining a little acidulated water, which they called *clyssus of nitre*, and attributed to it wonderful medical virtues. These mixtures of nitre and charcoal form the basis of a variety of compositions used for fire-works, the rapidity of the combustion being modified by the relative proportion of the charcoal.

When phosphorus is thrown upon nitre, and inflamed, a vivid combustion ensues, and a phosphate of potassa is formed. Sulphur sprinkled upon hot nitre burns, and produces a mixture of sulphate and sulphite of potassa. This salt used formerly to be employed in medicine, under the name of *Glaser's polychrest salt*. The combustion of a mixture of

nitre and sulphur has already been described as the source of sulphuric acid (p. 42.) When a mixture of two parts of nitre and one of muriate of ammonia are heated to redness, chloride of potassium, water, chlorine, muriatic acid, and a little nitrous acid, are the results, and nitrogen gas is copiously evolved. (Soubeiran, *Journal de Pharmacie*, 1827, p. 321.) Most of the metals, when in filings or powder, detonate and burn when thrown on red-hot nitre; some of the more inflammable metals produce in this way a considerable explosion.

A mixture of three parts of nitre, two of dry subcarbonate of potassa, and one of sulphur, forms *fulminating powder*. If a little of this compound be heated upon a metallic plate, it blackens, fuses, and explodes with much violence, in consequence of the rapid action of the sulphur upon the nitre, and the sudden evolution of nitrogen in its gaseous form.

GUNPOWDER consists of a very intimate mixture of nitre, sulphur, and charcoal, the proportions varying, according to the uses made of it, as follow:

	Common gunpowder.	Shooting powder.	Shooting powder.	Miners' powder.
Saltpetre . . . . .	75.0	78	76	65
Charcoal . . . . .	12.5	12	15	15
Sulphur . . . . .	12.5	10	9	20

The following is a table of the composition of gunpowder of several countries.

	Nitre.	Charcoal.	Sulphur.
Waltham Abbey mills . . . . .	75	15	10
France, national establishment . . . . .	75	12.5	12.5
———, for sportsmen . . . . .	78	12	10
———, for mining . . . . .	65	15	20
United States of America . . . . .	75	12.5	12.5
Prussia . . . . .	75	12.5	12.5
Russia . . . . .	73.78	13.59	12.63
Austria . . . . .	76	11.5	12.5
Spain . . . . .	76.47	10.78	12.75
Switzerland (round powder) . . . . .	76	14	10
Chinese . . . . .	75	14.4	9.9

The ingredients are *perfectly* mixed, moistened, beaten into a cake which is afterwards broken up, granulated, dried, and for the finest powder polished by attrition. The violence of the explosion of gunpowder depends upon the sudden production of gaseous matter, and of intense heat, resulting from the action of the combustibles upon the nitre. Carbonic oxide, carbonic acid, nitrogen, and sulphurous acid, are the principal gaseous results; and the solid residue consists of carbonate, sulphate, and sulphuret of potassa, and charcoal. (Cruikshanks, *Nicholson's Journal*, iv. See also the same *Journal*, xiii., 277.)

If we theoretically inquire how the maximum gaseous volume is to be produced from the chemical reaction of the elements of gunpowder, we shall find it to be by the generation of carbonic oxide and sulphurous acid, with the disengagement of nitrogen. This will lead to the following proportions of their constituents. (Ure, *Journal Royal Institution*, vol. i., p. 135.)

			Per cent.
1	prime equivalent of nitre	102	75.00
1	„ sulphur	16	11.77
3	„ charcoal	18	13.23
		<hr/>	<hr/>
		136	100.00

The nitre contains 5 proportionals of oxygen, of which 3 combining with 3 of charcoal will furnish 3 of carbonic oxide gas, while the remaining 2 will convert the 1 of sulphur into sulphurous acid gas: the single proportional of nitrogen is, therefore, in this view disengaged alone. The gaseous volume, on this supposition, evolved from 130 grains of gunpowder, equivalent in bulk to 75.5 grains of water, or to three-tenths of a cubic inch, will be at the atmospheric temperature as follows:

	Grains.	Cubic Inches.
Carbonic oxide	42	141.6
Sulphurous acid	32	47.2
Nitrogen	14	47.4
		<hr/>
		236.2

Being an expansion of one volume into 787.3. But as the temperature of the gases at the instant of their combustive formation must be incandescent, this volume may be safely estimated at three times the above amount, or considerably above two thousand times the bulk of the solid.

This theoretical account of the gases developed does not exactly accord with the experimental products usually assigned, especially as relates to the evolution of carbonic acid; carburetted and sulphuretted hydrogen, and vapour of water, often mentioned among the products of the combustion of gunpowder, are found in very minute quantities only, for good gunpowder does not contain more than 1 *per cent.* of water, which can be the only source of hydrogenated compounds. The larger the proportion of sulphur the less forcible will be the explosion of the powder; thus, when it contains 12 of charcoal and 12 of sulphur in 100, it does not throw a proof-shell so far as that containing 19 of charcoal and 9 of sulphur. But the former powder keeps better than the latter, so that for the supply of remote colonies and humid climates, it perhaps justifies a slight sacrifice of strength, which may be compensated by a larger charge.

There is a good account of the manufacture of gunpowder by Mr. Coleman, in the *Philosophical Magazine*, vol. ix., and in Aikin's *Dictionary of Chemistry*, (article, GUNPOWDER.) The strength and goodness of gunpowder is most accurately determined by measuring its actual projectile force by the *éprouvette*, which is a small strong barrel in which a given quantity of it is fired, and the force of expansion measured by the action exerted on a strong spring or a great weight. Another method is, to fire a heavy ball from a short mortar, with a given weight of the powder, and to find the range of projection. The *éprouvette*, formerly used in France, was a mortar seven inches (French) in calibre, which, with three ounces of powder, should throw a copper globe of 60 lbs. weight to the distance of 300 feet. Gunpowder is sometimes tried by placing two heaps of about sixty grains each upon clean writing-paper, three or four inches asunder, and firing one of them by a red-hot wire:

if the flame ascends quickly with a good report, sending up a ring of white smoke, leaving the paper free from white specks and not burnt into holes, and if no sparks fly off from it so as to set fire to the contiguous heap, the powder is very good; if otherwise, the ingredients are badly mixed or impure. It appears from Count Rumford's experiments on the force of gunpowder, (*Phil. Trans.*, LXXXVII., 254,) that 28 grains, confined in a cylindrical space which it just filled, tore asunder a piece of iron which would have resisted a strain of 400,000 lbs.

Gunpowder may, it is said, be inflamed by a violent blow; if mixed with powdered glass, or any other harder substance, and struck with a heavy hammer upon an anvil, it almost always explodes. It readily burns under water, and by using a slowly burning powder, such as squibs are filled with, inflamed in a tube of copper, the gaseous products may be collected over water in the pneumatic trough. The portfires used by the artillery answer very well for this experiment.

*Analysis of Gunpowder.* To analyze this compound, boil it with four parts of water, edulcorate the residue, dry it at  $212^{\circ}$ , and weigh; the loss indicates the nitre. The dry residue, composed of charcoal and sulphur, may be decomposed by spreading it upon an earthen plate, and burning off the sulphur at the lowest possible heat; the charcoal will remain, still however retaining a little sulphur. A more accurate process consists in introducing the mixture into a small retort furnished with a stop-cock, exhausted, and filled with chlorine; heat applied volatilizes the chloride of sulphur and leaves the charcoal, which may be washed, dried, and weighed. Another mode of analyzing gunpowder consists in separating the nitre by water, evaporating to dryness, and fusing the salt. To obtain the sulphur, 5 grains of the powder, 5 of carbonate of potassa, 5 of nitre, and 20 of pure common salt, are to be intimately mixed, and placed on the fire in a platinum vessel; the sulphur is slowly acidified, and when the mass becomes white it is dissolved in water, saturated with nitric or muriatic acid, and muriate of baryta added, so long as it occasions a precipitate; the sulphate of baryta thrown down is then collected, washed, and ignited, and its weight indicates the quantity of sulphur contained in the gunpowder by the usual computation. (Gay Lussac, *Ann. de Chim. et Phys.*, xvi., 437.)

**ACTION OF POTASSIUM ON AMMONIA.** This has been examined by Gay Lussac and Thenard, and by Sir H. Davy. When potassium is heated in ammonia, a fusible olive-coloured substance is obtained, of a crystallized fracture, translucent at the edges, heavier than water, and a non-conductor of electricity. It fuses at a little above  $212^{\circ}$ . It burns in oxygen, producing hydrated potassa and nitrogen: exposed to air, it slowly deliquesces, and evolves ammonia: water rapidly acts upon it, producing potassa and ammonia. The nature of this compound is not clearly understood: Gay Lussac and Thenard consider it as a compound of nitrogen, potassium, and ammonia; for hydrogen is evolved during its production. They found that a quantity of potassium which evolved one measure of hydrogen from water, absorbed from one to two measures of ammonia, (less at a high than a low temperature,) and evolved one measure of hydrogen.

**POTASSIUM AND SULPHUR.** When potassium and sulphur are heated

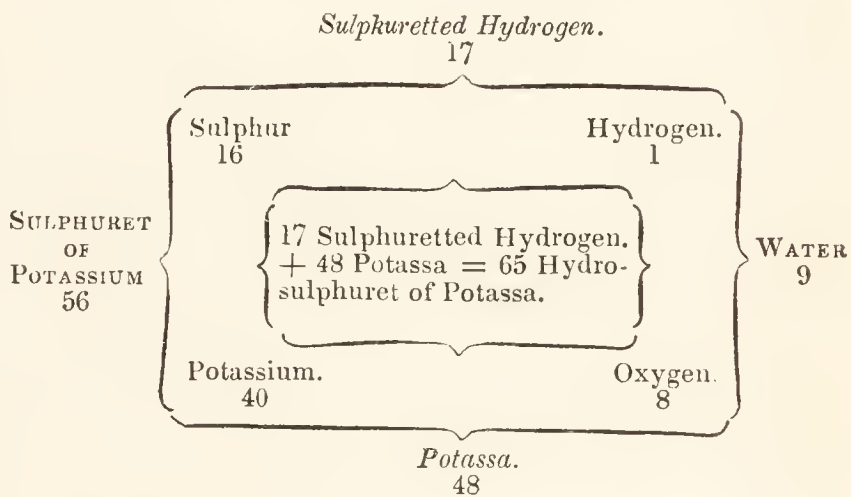


together in an exhausted tube, the sulphur not being in excess, intense action ensues, attended by the vivid combustion of the potassium, and a brownish-gray compound results: when proper proportions of the materials are used, this appears to be a true *sulphuret of potassium*, ( $po + s$ ).

The same compound is obtained by passing hydrogen through a red-hot tube containing sulphate of potassa: water is formed in consequence of the deoxidizement, by the hydrogen, of the acid and of the potassa. Thus procured it is a dark reddish-brown substance, not very inflammable, and deliquescent. It is fusible at a heat below redness, of a caustic and sulphureous taste, soluble in water and alcohol, and when heated by the blow-pipe, becomes incrustated with sulphate of potassa. From the mode of forming this compound it obviously consists of

Potassium	..	1	..	40	..	71.4
Sulphur	..	1	..	16	..	28.6
		1		56		100.0

When sulphuret of potassium is put into water it furnishes a solution of *hydrosulphuret of potassa* ( $p + o$ ) + ( $h + s$ ), in consequence of the decomposition of one proportional of water, by one of the sulphuret, as shown in the annexed diagram:—



A similar hydrosulphuret\* of potassa may be obtained by passing sulphuretted hydrogen through an aqueous solution of potassa, and if this be carefully evaporated in a retort so as to exclude air, it forms colourless prismatic crystals, which, independent of water of crystallization, may be considered as containing

Potassa	. . . . .	1	. .	48	. .	73.82
Sulphuretted hydrogen	. .	1	. .	17	. .	26.18
		1		65		100.00

HYDROSULPHURET OF POTASSIUM. ( $p + h + s$ ). When potassium is heated in sulphuretted hydrogen gas it burns, and the gas diminishes in volume. During this action the potassium decomposes one proportional of the gas, and combines with its sulphur to form sulphuret of potassium, which, uniting without decomposition with another proportional of the gas, forms a compound of

Sulphuret of potassium	. .	1	. .	56	. .	76.75
Sulphuretted hydrogen	. .	1	. .	17	. .	23.25
		1		73		100.00

\* Berzelius does not admit the decomposition of water in these cases of the solution of sulphurets of potassium, but considers the solution as containing the undecomposed sulphuret.

It is to such compounds that the term *sulphur salts* properly applies. This hydrosulphuret yields with water a colourless solution of bihydrosulphuret of potassa  $(p+o) + 2(h+s)$ . With dilute acids it evolves two volumes of sulphuretted hydrogen. When dilute acids are dropped into a solution of the hydrosulphuret, one volume of sulphuretted hydrogen is evolved, and no sulphur precipitated: when the solution is exposed to air, it absorbs oxygen, and becomes converted into hyposulphite of potassa.

**BISULPHURET OF POTASSIUM.**  $(p + 2s)$  When 4 parts of potassium are heated with 3 of sulphur, a brown fusible crystalline substance is obtained, permanent at a red heat, and consisting of

Potassium	. .	1	. .	40	. .	55.4
Sulphur	. .	2	. .	32	. .	44.6
		1		72		100.0

Acting upon water this compound decomposes one proportional of that fluid, and forms a yellow solution of sulphuretted hydrosulphuret of potassa, or of a compound of potassa with bisulphuretted hydrogen  $(p+o) + (2s+h)$  as in the annexed diagram.

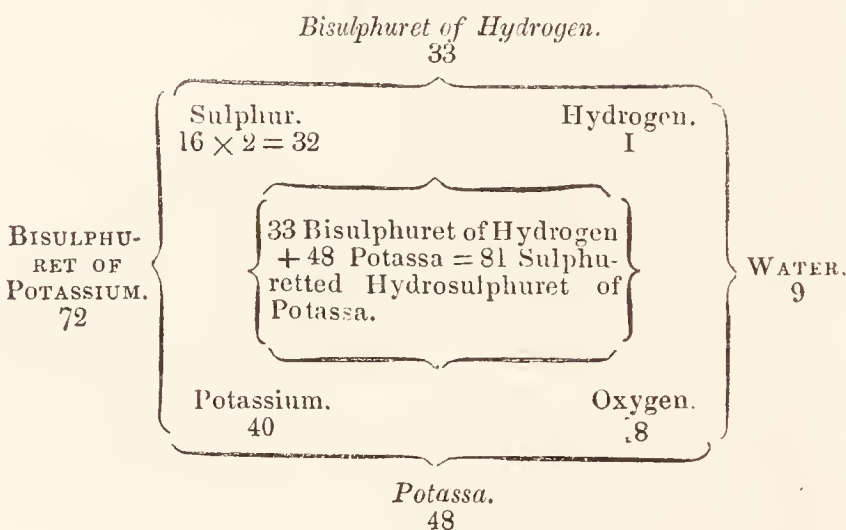
The solution therefore contains

Potassa	. . . . .	1	. .	48	. .	59.2
Bisulphuret of hydrogen	. .	1	. .	33	. .	40.8
		1		81		100.0

When the dilute acids are added to this aqueous solution, sulphuretted hydrogen is evolved and sulphur precipitated; but if a *strong* solution of it be poured into muriatic acid, a viscid substance falls, which is bisulphuretted hydrogen (see page 436.) Exposed to air, this solution passes into a hyposulphite, and sulphur is deposited.

It appears that the above are the only two definite compounds of sulphur and potassium; they are both permanent at high temperatures; but these unite indefinitely with sulphur by fusion at a moderate heat. Berzelius describes seven sulphurets of potassium, in which one proportional of metal is combined respectively with 1, 2, 3,  $3\frac{1}{2}$ , 4,  $4\frac{1}{2}$ , and 5 proportionals of sulphur (*Ann de Philos., N.S., iv., 214*), but the definite nature of these compounds seems open to some doubt.

**POTASSA AND SULPHUR.** When sulphur is fused with hydrate of potassa, the water of the hydrate evaporates, and the oxide of potassium is decomposed, giving rise, at a red heat, to sulphuret or bisulphuret of potassium (according to the quantity of sulphur used), and to hyposulphite (which becomes sulphate) of potassa. It does not appear that any sulphurous acid is in these cases evolved.



When carbonate of potassa and sulphur are heated together, carbonic acid is evolved, and the potassa and the sulphur act upon each other as just described; the result being, if air be not carefully excluded, sulphuret of potassium and sulphate of potassa.

The compounds thus obtained, by fusing potassa, or its carbonate with sulphur, were formerly designated *Livers of Sulphur*, in consequence of their colour; and the conversion of sulphate of potassa into liver of sulphur by the action of charcoal and heat, was an experiment instituted by Stahl in support of the phlogistic hypothesis. Exposed to air, these sulphurets deliquesce, and exhale a disagreeable smell; their taste is bitter, acrid, and nauseous. The general results of dissolving them in water, by which hydrosulphurets of potassa are obtained, have been above noticed.

When sulphur is boiled with the hydrosulphuret, or when excess of sulphur is boiled in solution of potassa, bihydrosulphuret of potassa may be obtained; but as this compound, when in solution, dissolves variable and apparently indefinite portions of sulphur, an uniform combination is not in this way easily obtainable.

HYPOSULPHITE OF POTASSA ( $PO + O$ ) + ( $2 S + 2 O$ ) or ( $P + \underline{S}$ ) is formed by decomposing hydrosulphuret of potassa by sulphurous acid and evaporating to a pellicle, when it forms acicular crystals, of a cooling, bitter taste, and deliquescent. After careful drying it takes fire upon elevating the temperature, and burns like tinder. Its solution readily dissolves moist chloride of silver; and when exposed to air becomes sulphite, and ultimately sulphate, of potassa. This salt is also formed when the alcoholic solution of sulphuret of potassium is exposed to air, and the adhering sulphuret washed from its crystals by alcohol: or by boiling a solution of sulphite of potassa with sulphur.

SULPHITE OF POTASSA ( $P + \underline{S}$ ) is formed by passing sulphurous acid into a solution of potassa, or of its carbonate, and evaporating out of the contact of air. Rhomboidal plates or prisms are obtained, white, anhydrous, of a sulphurous taste, and soluble in about their weight of water. By exposure to air, they pass into sulphate of potassa. Berzelius observes, that there is a bisulphite of potassa, more easily crystallizable than the sulphite, and generally confounded with it.

Sulphite of potassa consists of

Potassa	.	.	1	..	48	∴	60
Sulphurous acid	.	.	1	..	32	∴	40
			<hr/>		<hr/>		<hr/>
			1		80		100

HYPOSULPHATE OF POTASSA ( $PO + O$ ) + ( $2 S + 5 O$ ) or  $P + \underline{S'}$  is obtained by decomposing a solution of hyposulphate of baryta by sulphate of potassa. It forms permanent crystals of a bitter taste, difficultly soluble in cold, but readily so in hot water. It is anhydrous. Its crystals are described by Mr. Levy in the *Quarterly Journal*, xv., 285.

Hyposulphate of potassa consists, according to Heeren (*Ann. de Chim. et Phys.*, XL., 30) of

Potassa	.	.	1	..	48	∴	40
Hyposulphuric acid	.	.	1	..	72	∴	60
			<hr/>		<hr/>		<hr/>
			1		120		100

SULPHATE OF POTASSA  $(po + o) + (s + 3 o)$  or  $(P + S')$ . This salt is the result of several chemical operations carried on upon a large scale in the processes of the arts. It may be formed directly by saturating sulphuric acid by carbonate of potassa. It is the *sal de duobus*, and *arcanum duplicatum*, of the old chemists: the *potassæ sulphas* of the *London Pharmacopœia*. Its taste is bitter and saline. It crystallizes in short six-sided prisms, terminated by six-sided pyramids. The body of the prism is often wanting, and the triangular-faced dodecaëdron results. These forms have been particularly described by Mr. Levy, (*Quarterly Journal*, xv., 285). According to Mitscherlich its primitive form is a rhombic octoëdron, and it is isomorphous with seleniate, and also with chromate of potassa. The crystals, whilst forming, sometimes emit a yellow light. They are anhydrous. This salt dissolves in 16 parts of cold, and 5 of boiling water; or, according to Gay Lussac, 100 parts of water at  $32^\circ$  dissolve 8.36 of this salt, and for each degree above  $32^\circ$ , it takes up 0.1741 parts in addition; in consequence of its difficult solubility, it is thrown down in a white granular powder, when sulphuric acid is added to a moderately strong solution of potassa. It is insoluble in alcohol. Exposed to a red heat, it decrepitates and melts, but is not decomposed. At very high temperatures it is volatilized. It is decomposed at a red heat by hydrogen, which carries away the oxygen both of the acid and of the potassa, and converts it into sulphuret of potassium. When fused with sulphur, this salt undergoes no change; the sulphur sublimes unaltered. (Vauquelin, *Ann. de Chim. et Phys.*, v., 20.) Intensely heated with one-fifth its weight of powdered charcoal, it produces sulphuret of potassium. When about 2 parts of sulphate of potassa and 1 of lamp-black, intimately mixed in fine powder, are heated to redness in a coated phial, and great care taken to exclude the air during cooling, a compound is obtained which takes fire upon exposure to air. It appears to contain a compound of potassium, which powerfully attracts oxygen, and thus excites heat enough to inflame the charcoal and sulphur. Gay Lussac attributes the combustibility of common pyrophorus (see ALUMINA) to the presence of this compound.

Sulphate of potassa consists of

						Kirwan.	Dalton.	
Potassa	.	1	..	48	..	54.5	.. 55	.. 55.3
Sulphuric acid	.	1	..	40	..	45.5	.. 45	.. 44.7
		1		88		100.0		100.0

BISULPHATE OR SUPERSULPHATE OF POTASSA  $(po + o) + 2 (s + 3 o)$  or  $(P + 2 S')$  is formed by adding sulphuric acid to a hot solution of sulphate of potassa; or by boiling sulphate of potassa with half its weight of sulphuric acid in a platinum crucible, till none of the acid escapes when the heat approaches redness: the saline mass, dissolved and evaporated, furnishes crystals which affect various forms dependent upon the circumstances under which they are obtained: sometimes they present an acicular mass; at other times they are tabular; and sometimes flattened prisms.

According to Geiger they consist of

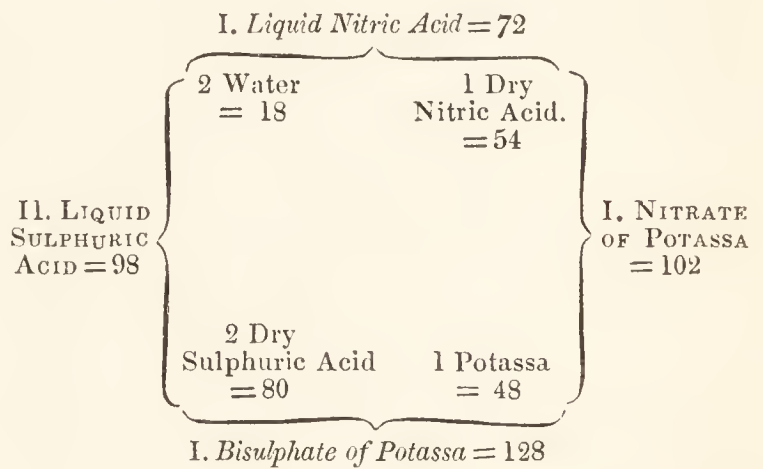
					Acicular.	Prismatic.
Potassa . . . . .	1	..	48	..	32.9	.. 33.83
Sulphuric acid . . . . .	2	..	80	..	54.8	.. 54.77
Water . . . . .	2	..	18	..	12.3	.. 10.74
	<hr/>		<hr/>		<hr/>	<hr/>
	1		146		100.0	100.00

The crystals of bisulphate of potassa are soluble in about half their weight of boiling water, and twice their weight of water at 40°. When dissolved in a large quantity of water and evaporated, crystals of sulphate of potash are deposited from a sour mother-liquor.

By a continued red heat this salt loses its excess of acid. Alcohol added to its aqueous solution throws down neutral sulphate of potassa.

Bisulphate of potassa (probably anhydrous) is also formed in the distillation of equal parts of nitre and sulphuric acid: nitric acid passes over, and a residuary bisulphate of potassa is produced, commonly known under the name of *sal enixum*\*. It is the *arcanum duplicatum*, or *panacea Holsatica* of old pharmacologists. It is used for cleansing coin and other works in metal; and has a place in some *Pharmacopœiæ*.

The annexed diagram will illustrate the formation of this salt, and of liquid nitric acid, in the distillation of two proportionals of sulphuric acid with one of nitre:—



SESQUISULPHATE OF POTASSA. (P + 1½S') This salt has been described and analyzed by Mr. Phillips (*Phil. Mag., N.S., ii., 420*): he obtained it as the residue of the distillation of equal weights of nitre and sulphuric acid (sp. gr. 1.8442). It was in filamentous crystals, and consisted of

Potassa . . . . .	2	..	96	..	42.60
Sulphuric acid . . . . .	3	..	120	..	54.57
Water . . . . .	1	..	9	..	2.83
	<hr/>		<hr/>		<hr/>
	1		225		100.00

AMMONIO-SULPHATE OF POTASSA (P + A + 2S') is obtained by adding ammonia to bisulphate of potassa, or by mixing solutions of sulphate of ammonia and sulphate of potassa, and setting aside to crystallize: it forms transparent prisms of a bitter taste: 100 of water at 60° dissolve 13. (*LINK, Crell's Annals, 1796.*) It consists of

Sulphate of potassa . . . . .	1	..	88	..	48.6
Sulphate of ammonia . . . . .	1	..	57	..	31.5
Water . . . . .	4	..	36	..	19.9
	<hr/>		<hr/>		<hr/>
	1		181		100.0

PHOSPHURET OF POTASSIUM (po + p) is a chocolate-brown compound, which rapidly decomposes water, evolving phosphuretted hydrogen gas. It is formed by cautiously heating potassium with phosphorus out of the

\* This salt, from the variable quantity of nitric acid, is generally a mixture of sulphuric acid used in the distillation | sulphate and bisulphate of potassa.

contact of air; or by decomposing phosphuretted hydrogen by potassium, which, when heated in that gas, forms this phosphuret and evolves pure hydrogen.

When heated with potassium it appears capable of combining with an additional proportion of that substance, and forms a lead-coloured compound, in which it is probable that 2 proportionals of potassium are combined with 1 of phosphorus.

By heating potassium with glacial phosphoric acid, Gay Lussac and Thenard obtained a brown compound which decomposed water: it was probably a mixture of phosphuret of potassium and phosphate of potassa.

**HYPHOPHOSPHITE OF POTASSA** ( $po + o$ ) + ( $2p + o$ ) or ( $P + \underline{p}$ ) has been examined by Dulong. It is very deliquescent, and soluble in water and alcohol nearly in all proportions. When heated it evolves phosphuretted hydrogen and phosphorus, and is converted into phosphate of potassa. (*Ann. de Chim. et Phys.*, ii., 142.) It is best prepared by mixing a solution of hypophosphite of lime with one of carbonate of potassa, filtering, and evaporating to dryness: alcohol, digested upon the residue, takes up the hypophosphite of potassa: it is uncrystallizable, but may be dried in vacuo. (Rose, *Quarterly Journal*, iv., 206.) The substance described by Grotthus (*Ann. de Chim.*, LXIV., 20), as resulting from the action of phosphorus upon a solution of potassa, is probably this hypophosphite.

**PHOSPHITE OF POTASSA** ( $po + o$ ) + ( $p + 1\frac{1}{2}o$ ) or ( $P + \underline{p}$ ) is a soluble deliquescent uncrystallizable salt, insoluble in alcohol (Dulong).

**PHOSPHATE OF POTASSA** ( $po + o$ ) + ( $p + 2\frac{1}{2}o$ ) or ( $P + p'$ ) is a soluble difficultly-crystallizable salt, of a cooling urinous taste, formed by adding carbonate of potassa to hot phosphoric acid till the solution ceases to affect vegetable blues. It is insoluble in alcohol. It may be obtained by very careful evaporation, in four-sided prisms, and octoëdrons, composed according to Thomson, of

Potassa	.	.	1	..	48	..	51.6
Phosphoric acid	.	.	1	..	36	..	38.7
Water	.	.	1	..	9	..	9.7
			1		93		100.0

**DIPHOSPHATE OF POTASSA**; ( $2P + p'$ ) is formed by adding hydrate of potassa to the *phosphate*, and removing the excess of alkali by alcohol, when the basic salt (diphosphate) falls in the form of an oily liquid. (Berzelius.) It may also be obtained by adding hydrate of potassa to a solution of the phosphate, *evaporating to dryness*, and then removing the excess of potash by alcohol: it is tasteless, insoluble in cold water, but soluble in hot water, and precipitates as the solution cools, in the form of a gritty powder: it is extremely fusible: it is soluble in nitric, muriatic, and phosphoric acids, and the solutions are glutinous; when sufficiently diluted, the alkalis occasion no precipitate in these solutions. (Thomson.)

It consists of

Potassa	.	.	2	.	.	96	.	.	72.75
Phosphoric Acid	.	.	1	.	.	36	.	.	27.25
			1			132			100.00

BIPHOSPHATE OF POTASSA ( $P + 2p'$ ) is formed by dissolving the neutral phosphate in phosphoric acid, and evaporating till crystals are obtained, which are prismatic and very soluble in water, but insoluble in alcohol. According to Mitscherlich (*Ann. de Chim. et Phys.*, xix., 364), the biphosphate of potassa consists of

						Mitscherlich.
Potassa . . .	1	..	48	..	34.8	.. 34.40
Phosphoric acid	2	..	72	..	52.2	.. 52.48
Water . . .	2	..	18	..	13.0	.. 13.12
	1		138		100.0	100.00

POTASSIUM AND SELENIUM. ( $po + se$ .) When these substances are heated together, they combine with intense action, and produce a gray crystalline compound, forming a deep-brown solution with water, from which acids evolve seleniuretted hydrogen and precipitate selenium. When selenium is heated with excess of potassium, an explosion ensues, and a compound is obtained which furnishes a red solution, and evolves hydrogen by the action of water. The odour and general characters of these compounds so much resemble those with sulphur, as not easily to be distinguished except by the brown and red colours of their solutions.

When powdered selenium is boiled in solution of potassa, a dark-brown solution of an hepatic taste and smell is the result, from which acids precipitate selenium. Fused with potassa, selenium produces seleniate of potassa and seleniuret of potassium.

POTASSA AND SELENIOUS ACID form, according to Berzelius, a neutral *selenite of potassa* ( $po + o$ ) + ( $se + 2o$ ) or ( $P + se$ ), a *biselenite* ( $P + 2se$ ), and a *quadriselenite* ( $P + 4se$ ). The first is difficultly crystallizable, somewhat deliquescent, and insoluble in alcohol. The second forms plumose crystals, very sparingly soluble in alcohol. The third is uncrystallizable. (*Ann. de Chim. et Phys.*, ix., 257.)

SELENIATE OF POTASSA. ( $po + o$ ) + ( $se + 3o$ ) or ( $P + se'$ .) This salt may be obtained by fusing nitre with selenium or selenious acid, or by saturating the selenic acid by potassa. From the statement of Mitscherlich it consists of

Potassa . . .	1	..	48	..	42.9
Selenic Acid . . .	1	..	64	..	57.1
	1		112		100.0

According to the same authority, the seleniates and the sulphates are isomorphous. (*Ann. de Chim. et Phys.*, xxxvi., 104.)

POTASSIUM AND CARBON. When potassa is decomposed at high temperatures by carbon, a black substance remains in the retort, which is probably a *carburet of Potassium*. ( $po + car$ .) It takes fire upon water; and if plunged into that fluid evolves carburetted hydrogen. It is probable that several of the pyrophoric charcoals contain potassium.

POTASSA AND CARBONIC ACID. These bodies combine in two proportions, forming the *carbonate* and the *bicarbonate* of potassa, compounds which have been long used and known under various names; such as *fixed nitre*, *salt of tartar*, *salt of wormwood*, *vegetable alkali*, &c. Their composition was first ascertained by Black. Bergman, in 1774, described their most essential properties. (*Opuscula*, vol. i., p. 13.)

CARBONATE OF POTASSA  $(po+o)+(car+2o)$  or  $P+car'$ , is a salt of great importance in many arts and manufactures, and is known in commerce in different states of purity, under the names of *wood-ash*, *pot-ash*, and *pearl-ash*. It is the *subcarbonate of potassa* of the *London Pharmacopœia*.

It may be obtained directly, by passing carbonic acid into a solution of potassa, till saturated, evaporating to dryness, and exposing the dry mass to a red-heat; or indirectly, by burning *tartar*, lixiviating the residue, and evaporating to dryness, whence the name *salt of tartar* has been applied to it.

Carbonate of potassa is fusible without decomposition, at a red-heat; its specific gravity is 2.6; it is very soluble in water, which at  $55^{\circ}$  takes up about its own weight; it deliquesces by exposure to air, forming a dense solution, once called *oil of tartar per deliquium*. Its taste is alkaline, and it renders vegetable blues green. It consists, in its fused or anhydrous state, of

					Vauquelin.	Dalton.	
Potassa . . . . .	1	..	48	..	68.5	.. 67	.. 68.9
Carbonic Acid	1	..	22	..	31.5	.. 33	.. 31.1
	<hr/>		<hr/>		<hr/>	<hr/>	<hr/>
	1		70		100.0	100	100.

A saturated solution of carbonate of potassa in water contains about 48 per cent. of the salt, and has a specific gravity of 1.5. The following table, showing the quantity of dry carbonate of potassa in solutions of different specific gravities, is by Richter. (Gmelin, i., 2 abt., p. 530, Ed. 1827.)

S. G.	Per Cent.	S. G.	Per Cent.	S. G.	Per Cent.
1.58	--- 37.4	1.38	--- 27.0	1.18	--- 13.5
1.56	--- 36.5	1.36	--- 26.0	1.16	--- 12.0
1.54	--- 35.4	1.34	--- 24.5	1.14	--- 10.6
1.52	--- 34.1	1.32	--- 22.7	1.12	--- 9.4
1.50	--- 32.7	1.30	--- 20.8	1.10	--- 8.2
1.48	--- 31.8	1.28	--- 19.7	1.08	--- 6.6
1.46	--- 30.9	1.26	--- 18.7	1.06	--- 4.9
1.44	--- 29.9	1.24	--- 17.5	1.04	--- 3.3
1.42	--- 29.0	1.22	--- 16.3	1.02	--- 1.7
1.40	--- 28.0	1.20	--- 15.1		

If a solution of this carbonate be evaporated till of a specific gravity of 1.62 whilst warm, and then poured into a tall cylindrical glass vessel, and suffered slowly to cool, it furnishes crystals in long rhomboidal tables, which are very deliquescent. The remaining mother-liquor, when cold, yields further crystals on evaporation, or when long kept: in the latter case the crystals are rhombic octoëdra. (Berard, *Ann. de Chim.*, lxxi., 50. Giese *Scherer's Annalen*, iv., 294). Fabbroni afterwards described these crystals, without being aware that they were previously known. (*Ann. de Chim. et Phys.*, xxv., 5.) They consist of

				Giese.	Berard.
Potassa . . . . .	1	..	48	.. 54.5	.. 55
Carbonic Acid . . . . .	1	..	22	.. 25.0	.. 25
Water . . . . .	2	..	18	.. 20.5	.. 20
	<hr/>		<hr/>	<hr/>	<hr/>
	1		88	100.0	100
					79.4
					20.6
					<hr/>
					100.0



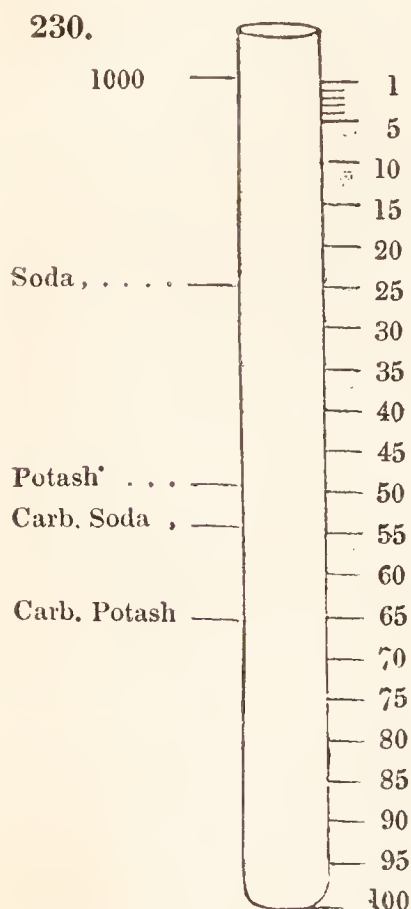
Carbonate of potassa is insoluble in alcohol, and is occasionally employed to deprive alcohol of water. Berzelius states, that if steam be passed over this salt in a red-hot tube, its carbonic acid is expelled, and hydrated potassa formed. A few of the metals, and charcoal at very high temperatures, decompose it with the production of potassium. The action of sulphur and of phosphorus upon this carbonate has already been noticed.

The great consumption of carbonate of potassa in various manufactures is exclusively supplied by the combustion of vegetables, and consequently its production is almost limited to those countries which require clearing of timber, or where there are vast natural forests. The English market is chiefly supplied from North America. If any vegetable, growing in a soil not impregnated with sea-salt be burned, its ashes will be found alkaline from the presence of carbonate of potassa. If the ashes be submitted to heat, so as to burn away the carbonaceous matter entirely, they become a white mass, generally termed *pearl-ash*.

The pearl-ash of commerce contains a variety of impurities, which render it of variable value. In general, its purity may be judged of by its easy solubility in water, two parts of which should entirely and easily dissolve one part of the salt, without the aid of heat; the residue, if any, consists of impurities. The quantity of nitric acid of a given density, requisite to saturate a given weight, may also be resorted to as a criterion of its purity. 100 parts of nitric acid, specific gravity 1.36, will saturate 65.7 parts of dry carbonate of potassa, which are equivalent to 45 parts of pure potassa; or, 355 grains of diluted sulphuric acid of the specific gravity 1.141 exactly neutralize 100 grains of pure carbonate of potassa. Hence, if we dissolve 100 grains of the alkali to be examined, in six or eight parts of water, and gradually add the test sulphuric acid till we find, by the application of violet or mallow paper, that the alkali is exactly neutralized, we may deduce, from the weight of the acid consumed, the proportion of real carbonate present: for as 355 is to 100, so is the weight of the test-acid employed to that of the pure carbonated alkali present. To save trouble, the acid properly diluted may be put into a glass tube, so graduated as to show directly the value of the alkali by the quantity consumed in its saturation. Thus we find, by reference to the scale of equivalents, that 100 parts of carbonate of potassa are saturated by 70 of sulphuric acid, specific gravity 1.85. If, therefore, we put 70 grains of such acid into a tube divided into 100 parts, and fill it up with water, it follows that the quantity of carbonate of potassa existing in any sample of pearl-ash under examination, will be directly shown by the measure of such diluted acid required for saturation; 100 grains of the sample, if pure carbonate, would require the whole 100 measures of acid: but if only containing 50 *per cent.* of pure carbonate, the 100 grains would be saturated by 50 measures of the test-acid, and so on. Such graduated tubes are sometimes called *alkalimeters*.

The following directions respecting their construction and use, I abstract from Mr. Faraday's *Manipulation*. Let a tube, closed at one end (fig. 230), of about three-fourths of an inch internal diameter, and nine inches and a half in length, have 1000 grains of water

weighed into it; then let the space it occupies be graduated into 100 equal parts, and every ten divisions numbered from above downwards. At 23.44 parts, or 76.56 parts from the bottom, make an extra line a little on one side, or even on the opposite side to the graduation,



and write at it with a scratching diamond *soda*; lower down at 48.96 parts, make another line, and write *potash*; still lower at 54.63 parts, a third line marked *carb. soda*; and at 65 parts a fourth, marked *carb. potash*. It will be observed that portions are measured off, beneath these marks, in the inverse order of the equivalent numbers of these substances, and consequently directly proportionate to the quantities of any particular acid, which will neutralize equal weights of the alkalies or their carbonates. As these points are of great importance, it will be proper to verify them by weighing into the tube first 350, then 453.7, then 510.4, and lastly 765.6 grains of water, which will correspond with the marks if they are correct. Or the graduation may be laid down from the surface of the four portions of fluid when weighed in, without reference to where they fall upon the general scale. The tube is now completed, except that it should be observed whether the aperture can be perfectly

and securely covered by the thumb of the left hand, and if not, or if there be reason to think it not ultimately secure, then it should be heated and contracted until sufficiently small.

Diluted sulphuric acid must now be prepared to be used with the tube. When of a specific gravity of 1.1268, it will be very nearly, if not accurately, of the strength required; and this may be obtained by mixing one part by weight of oil of vitriol of specific gravity 1.82, with four parts of water. If, when cold, the specific gravity of this diluted acid be as above mentioned 1.1268, it must be nearly, if not exactly, of the strength required; but before being admitted into use, should be examined experimentally. Assuming it, however, as being absolutely correct, it will be found that a quantity measured into the tube up to any one of the four marks described, is sufficient to neutralize 100 grains of the dry alkali or carbonate set down at the mark; consequently, if water be added in the tube, thus filled up to any one of the marks, until the 100 parts are full, and the whole uniformly mixed, one part of such diluted acid will neutralize one grain of the alkali or carbonate named at the mark, up to which the tube was first filled with the acid of specific gravity 1.1268.

When a specimen of potash, barilla, or kelp, is to be examined by this instrument, 100 grains are to be weighed out, dissolved in warm water, filtered, the insoluble portion washed, and the solution added to the rest; by this process the alkali will be separated from carbonate of lime, or other insoluble matters, which otherwise might cause errors in

the estimation. The alkaline solution is to be put into a basin on the sand-bath, and then the tube and acid prepared. For this purpose some of the acid, of specific gravity 1.1268 is to be poured into the tube until it rises up to the mark indicating the substance to be tested for; *potash* or *carbonate of potash* for the potash or pearlash of commerce, and *soda* or *carbonate of soda* for barilla or kelp: then water is to be added carefully, until the hundred parts are filled, and closing the tube with the finger, its contents are to be perfectly agitated and mixed.

The alkali in the basin is now to be neutralized with the acid in the tube. After having once placed the thumb of the left hand over the aperture of the tube, it is not to be again removed; but inverting the tube by turning the hand so that the thumb and the mouth of the tube are downwards, the acid is to be let out gradually into the alkaline solution, by relaxing the thumb and admitting a succession of small bubbles of air; the hot solution beneath is to be continually stirred, so as to mix the acid instantly with the whole, and the operator must proceed with increased caution as the point of neutralization is approached. Very small quantities of the acid may be added, by slightly relaxing the thumb so as to permit a minute quantity, less than a drop, to flow to its extremity, and touching it with the glass rod; the final adjustment may thus be made more accurately, than by dropping the acid from the lip of the tube. The process must be carried on until the alkali is found by the test-papers to have been exactly neutralized: then the tube must be inverted, the thumb removed, drawing its under surface over the edge of the tube, so as to leave as much as possible of the fluid that otherwise might adhere to it, and having allowed the sides to drain, it must be observed how many parts of acid have been used, the number of which will indicate the number of grains of the alkali or carbonate, contained in the 100 grains of the impure alkali operated with\*.

With respect to the proper strength of the acid, it is to be examined in the following manner: crystals of bicarbonate of potash are to be fused in a platina crucible, the fluid poured out upon a clean, cold metal plate, and a piece of the resulting solid, estimated to be 70, 80, or 100 grains, weighed in water; in this way a known weight of pure carbonate of potash will be obtained in solution. The solution is then to be diluted, heated, and neutralized by acid from the tube diluted as before described, from the mark of carbonate of potash. If it be found that as many parts of the acid have been used as of grains of the carbonate weighed out, the acid is of proper strength: if more acid has been used, it is too weak; if less has been sufficient, it is too strong. Suppose for instance that 100 grains of the salt (fused carbonate of potash) had been used, and that 90 parts of the acid were sufficient; then these 90 parts ought to have occupied the 100, and consequently the 100 parts contain

\* Some of the impure sources of potash and soda used in the arts, contain amongst other substances sulphuret and sulphite of alkali. Both these occasion errors in the mode of estimation above described, to obviate which MM. Welter and Gay Lussac (*Annales de Chimie*, xiii., 212) advise, that after the soluble parts have been separated by water, a little chlorate of potash should be added to them, the whole evaporated and heated to redness. This converts the sulphuret and sulphite into neutral sulphate, and then upon redissolving the whole, the caustic and carbonated alkali may be ascertained as above described.

one-tenth too much acid, in consequence of the experimental acid itself containing one-tenth more than it ought to do. Hence the latter must be diluted with such a quantity of water as will make nine volumes into ten, or by one-ninth its volume; for as the 90 parts used are to the 100 parts they ought to have occupied, so is any number of parts by volume of the acid under trial, to the number of parts which it ought to occupy. The difference between the two last numbers will give the quantity of water in volumes, to be added to the acid expressed by the first of them, in order to correct it and make it of proper strength. On the contrary, if it were found that the 100 parts were insufficient, and that 10 parts more of similar acid were required, then there is too much water by one-eleventh of the whole in bulk, the correction for which would be one tenth more of the 35 parts of acid put into the tube up to the mark 65 *carb. potassa*. This tenth is 3.5 parts, but as only a fifth of that or 0.7 parts is acid, therefore 0.7 parts by weight of the same oil of vitriol that was used before must be added for every 35 parts of the mixed acid. The correction in any other case may be easily made, by considering that the number of parts over a hundred which are necessary to saturate the 100 grains of carbonate of potash, are proportionate to the quantity of oil of vitriol which must be added to bring the experimental acid to proper strength: thus if 136 parts of the diluted acid were used, then thirty-six-hundredths more of the weight of oil of vitriol already used must be added; and the quantity of oil of vitriol that was added at first being known to be one-fifth by weight, the additional quantity required is easily ascertained. These corrections are not strictly accurate, but sufficiently so to meet even the exaggerated cases put of a difference of 10 parts, and to bring it within the limit of errors of experiment.

Sometimes instead of using test-papers, a little of the neutralized blue-cabbage liquor, or of infusion of litmus may be put into the alkaline solution; the former immediately assumes a green tint: and by attending to the change effected by the addition of the acid, and noticing the point when blueness is again restored to the cabbage-colour, or when the litmus becomes reddened, the indication of neutrality is sufficiently evident and accurate for general purposes. The test by papers is, however, more precise.

A process of neutralization, quite the same in principle, may be adopted for the purpose of estimating the strength of *acids*, but from circumstances it is not often used, and being easily comprehended from the above directions, claims no further notice here.

The common mode of purifying pearl-ash consists in pouring upon it its weight of cold water, and stirring the mixture occasionally during twenty-four hours; the solution is then poured clear off the residuary salt, and evaporated to dryness. In this way much impurity is separated, the foreign salts being, with few exceptions, much less soluble than the alkaline; yet some of them are taken up, and the silicated potassa which rough pearl-ash always contains, is also dissolved. The carbonate from tartar is more pure, but often contains lime. The purest carbonate is undoubtedly that obtained by exposing the crystallized bicarbonate to heat sufficient to expel its water and half of its carbonic acid; the salt is then dissolved in water, which generally leaves some silica, that has been rendered inso-

luble by the exposure to heat. If the salt be fused, this silica combines with the potassa and expels a portion of carbonic acid, so that although a certain degree of heat is required to drive off the excess of carbonic acid, and render the silica insoluble, too much heat causes it again to be taken up, and rendered soluble in water. With these precautions, upon evaporating the solution to dryness in a silver basin, a very pure carbonate of potassa is obtained. Carbonate of potassa is also obtained when two parts of powdered tartar (bitartrate of potassa) and one of nitrate of potassa, thoroughly mixed, are deflagrated in successive portions in an iron ladle or crucible. The residue (often called *black flux*) is lixiviated and evaporated as usual. Equal parts of nitre and tartar, treated in the same way, furnish *white flux*, in which the whole of the charcoal is destroyed by combustion. These fluxes are of much use in certain metallurgical operations, contributing to the fusibility of refractory earthy compounds.

BICARBONATE OF POTASSA ( $P + 2 CAR'$ ), is formed by passing a current of carbonic acid into a solution of the carbonate. By evaporation at a very moderate heat, crystals are obtained in the form of four-sided prisms, with diédral summits. They are not deliquescent. Their primitive form and cleavage have been described by Mr. Levy in the *Quarterly Journal*, xv. 286, and by Mr. Brooke (*Ann. of Phil., N.S.*, vi. 42.) Their taste is only slightly alkaline, and they require for solution four parts of water, at  $60^{\circ}$ . Boiling water dissolves nearly its own weight of the crystals, but during the solution a portion of carbonic acid is evolved. Exposed to a red-heat, they evolve carbonic acid and water, and carbonate of potassa remains. This salt was first observed by Dr. Wollaston to contain exactly twice the quantity of carbonic acid existing in the carbonate. (*Phil. Trans.* 1808.)

It contains, according to Berard, 9 per cent. of water. Crystallized bicarbonate of potassa, therefore, consists of

Potassa . . . 1	..	48	..	47.58	..	Berard.
Carbonic acid 2	..	44	..	43.60	..	48.92
Water . . . 1	..	9	..	8.82	..	42.01
		<hr/>		<hr/>		9.07
		1		100.00		100.00

The analyses of this salt by Kirwan and Pelletier would indicate two atoms of water.

It is generally stated that during the saturation of silicated carbonate of potassa with carbonic acid, the whole of the silica is precipitated; but this is not the case; and it will be found that during the crystallization of the salt, an additional deposition of silica ensues. When the crystals of bicarbonate have been redissolved, and a second time crystallized, the silica is excluded.

In the *London Pharmacopœia*, the more expensive method of obtaining this salt by the action of carbonate of ammonia on carbonate of potassa is resorted to.

The following proportions may be used for the preparation of bicarbonate of potassa upon the large scale: 100lbs. of purified carbonate of potassa are dissolved in 17 gallons of water, which, when saturated with

carbonic acid, yield from 35 to 40 lbs. of crystallized bicarbonate; 50 lbs. of carbonate of potassa are then added to the mother-liquor, with a sufficient quantity of water to make up 17 gallons, and the operation repeated\*.

The carbonate and bicarbonate of potassa are both decomposed by lime, which deprives them of carbonic acid; hence the use of that earth in the process for obtaining pure *potassa*. They are also decomposed by the greater number of acids, which unite with the alkali, the carbonic acid being expelled with effervescence.

**SESQUICARBONATE OF POTASSA.** When the solution of the bicarbonate is boiled until carbonic acid no longer escapes, it loses one-fourth of its acid, and on cooling, forms deliquescent crystals, insoluble in alcohol. The same salt is obtained by dissolving 100 parts of carbonate and 131 of bicarbonate of potassa in water. This salt was first mentioned by Berthollet in 1809 (Berzelius.) It is probably identical with that noticed by Dr. Thomson, (*Princip. of Chem.*, ii. 225,) who states it to consist of

Potassa . . .	1	. .	48	. .	35.55
Carbonic acid .	1½	. .	33	. .	24.45
Water . . .	6	. .	54	. .	40.00
	1		135		100.00

**POTASSIUM AND CYANOGEN.** Potassium heated in cyanogen absorbs the gas with vivid ignition, and produces a yellowish-gray *cyanuret of potassium*, ( $po + 2car + n$ ) which, by the action of water, becomes *hydrocyanate of potassa*. ( $po + o$ ) + ( $2car + n + h$ ). When cyanogen is passed into a solution of potassa, a liquid is obtained which, when the cyanogen is in excess, is brown and smells of the gas. This compound has been called cyanuret or cyanide of potassa.

When animal substances, such as horn or dried blood, are calcined at a red-heat, with half their weight of carbonate of potassa, so long as a blue flickering flame burns upon the surface, and after the mass has cooled, if it be lixiviated with a small quantity of water, a solution of carbonate with cyanuret of potassium is obtained, which, when filtered, precipitated with acetate of lime, again filtered, and mixed with alcohol, yields a precipitate of cyanuret of potassium.

Cyanuret of potassium may also be obtained by heating dried or anhydrous ferrocyanuret of potassium to redness in an iron bottle as long as it gives out gas: it is thus converted into carburet of iron and cyanuret of potassium; the latter should be dissolved in the smallest possible quan-

\* The *purified Carbonate of Potassa* of the shops should be perfectly soluble in twice its weight of cold water. It often contains *silica*, *sulphate of potassa*, *chloride of potassium*, and *carbonate of lime*. To detect these, dissolve a hundred grains in excess of nitric acid diluted with eight parts of water; the silica, if any be present, remains undissolved, or may be rendered insoluble by evaporation: separate the solution into three equal parts; to the first, add nitrate of

baryta, which causes a precipitate of sulphate; collect, wash, and dry it; 100 parts are equivalent to 74 of sulphate of potassa: to the second, add nitrate of silver; 100 grains of the precipitate, washed and dried at a dull red-heat, are equivalent to 52 of chloride of potassium: to the third, add oxalate of ammonia, and dry the edulcorated precipitate at a heat of 300°; 100 parts are equal to 77 of carbonate of lime.

tity of cold water, rapidly filtered with as little exposure to air as possible, and evaporated to dryness in vacuo over a surface of sulphuric acid.

Cyanuret of potassium should be carefully preserved out of the contact of air and water; it may be fused without decomposition, and after fusion often crystallizes in cubes: its taste is pungent and alkaline, accompanied with the flavour of hydrocyanic acid. It is very soluble in water, and very little soluble in absolute alcohol, so that the latter throws it down from its recent and cold aqueous solution: exposed to air it becomes moist and smells of hydrocyanic acid: it is very poisonous. Its solution is decomposed by the acids and by heat: the former resolve it into potassa and hydrocyanic acid: when heated its elements enter into new combinations producing ammonia, and carbonic and hydrocyanic acids.

CYANATE OF POTASSA ( $po + o$ ) + ( $2car + n + o$ ) is obtained by carefully heating a mixture of equal parts of dry ferrocyanuret of potassium, and peroxide of manganese to dull redness: when cold, the fused mass is powdered, and boiled in alcohol of 0.86, which dissolves the cyanate and deposits it on cooling. This salt is decomposed both by water and acids, which convert the cyanic acid into carbonic acid and ammonia (see p. 502). It crystallizes in small plates like chlorate of potassa; tastes like saltpetre; is anhydrous; and in close vessels excluded from air and moisture, may be fused without decomposition\*. When fused with potassium it yields a mixture of cyanuret of potassium and potassa; and with sulphur, a mixture of sulphocyanuret of potassium, sulphuret of potassium, and sulphate of potassa. Cyanate of potassa consists of

Potassa . . . . .	1	. .	48	. .	58.5	. .	Wöhler.
Cyanic acid	1	. .	34	. .	41.5	. .	57.95
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>		<hr style="width: 100%;"/>		<hr style="width: 100%;"/>
	1		82		100.0		100.00

SULPHOCYANURET OF POTASSIUM ( $po + n + 2car + 2s.$ ) When 5 parts of dry ferrocyanuret of potassium, 5 of sulphur, and 1 of carbonate of potassa are well mixed in fine powder and exposed to nearly a red-heat, the mixture fuses and takes fire; it should be stirred as long as it continues to burn, and kept for a few minutes in fusion. The residue, digested in hot water and filtered, furnishes a solution, which, evaporated to dryness, affords *sulphocyanuret of potassium*; sulphuret of iron remains upon the filter. The sulphocyanuret may be purified by digestion in alcohol, which dissolves it, and leaves any carbonate of potassa that might have been mixed with it. The alcoholic solution when evaporated, leaves the pure salt, which, redissolved in water and concentrated by evaporation, yields prismatic crystals which are of a cooling, saline taste, deliquescent and anhydrous, being in form, taste, and fusibility, very analogous to nitre.

Whether, when dissolved in water, this salt is to be considered as sulphocyanate of potassa, is a question similar to that which applies to the analogous conversion of the chlorides into muriates, and of the sulphurets into hydrosulphates. Distilled with phosphoric acid, the sulphocyanic acid passes over, and phosphate of potassa remains in the retort. Its aqueous solution is a delicate test of the presence of peroxide of iron, which it

\* WÖHLER (*Ann de Chim. et Phys.*, xx. 353, and xxvii. 196.)

throws down of a blood-red colour; and the solution of the sulphocyanuret often acquires a pinkish tinge from the presence of a trace of iron.

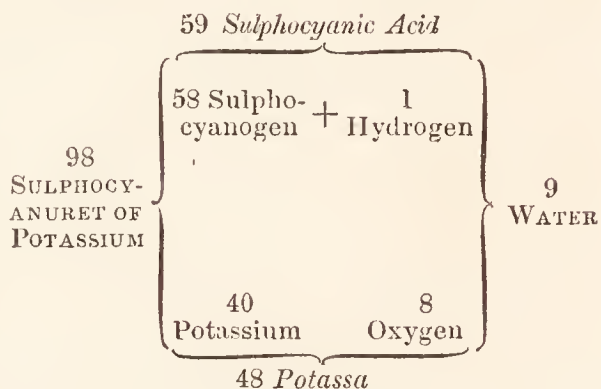
Sulphocyanuret of potassium is a compound of

						Berzelius.
Potassium . . .	1	..	40	..	40.8	.. 40.33
Sulphocyanogen	1	..	58	..	59.2	.. 59.67
	1		98		100.0	100.00

Its ultimate constituents, therefore, are

Potassium . . .	1	..	40	..	40.8
Sulphur . . .	2	..	32	..	32.7
Nitrogen . . .	1	..	14	..	14.3
Carbon . . .	2	..	12	..	12.2
	1		98		100.0

And assuming that, by the action of water, the potassium forms potassa, and sulphocyanogen sulphocyanic (or rather hydrosulphocyanic) acid, then the annexed diagram will represent the change.



**SELENIOCYANURET OF POTASSIUM.** ( $po + n + 2 car + 2 se.$ ) Berzelius formed this salt by heating a mixture of ferrocyanuret of potassium and selenium, and washing the fused mixture: by evaporation, anhydrous crystals of the *seleniocyanuret* were obtained.

**POTASSIUM AND BORON.** When boracic acid is reduced by fusion with potassium, a brown mass results, which evolves hydrogen in water; probably, however, only from adhering potassium.

**BORATE OF POTASSA,** ( $P + bo'$ ), is a salt which has been scarcely examined: it may be prepared by boiling boracic acid in solution of potassa, or by exposing a mixture of boracic acid and nitre to a bright red heat; it furnishes by solution and evaporation quadrangular prisms, permanent in the air. It combines with excess of base to form a *diborate*.

**BOROFLUORIDE OF POTASSIUM** is obtained, according to Berzelius, by adding fluoboric acid to a solution of fluoride of potassium: a gelatinous precipitate ensues, which, collected upon a filter, becomes opaque, and feels, whilst moist, like powdered starch. When dry, it has a bitterish taste: it does not redden litmus. 100 parts of cold water only dissolve 1.4 of this salt; but it is more soluble in boiling water, and, as the solution cools, it deposits it in small anhydrous crystals. It requires a high heat, long continued, for its decomposition, and is ultimately resolved into fluoboric gas and fluoride of potassium.

**THE SALTS OF POTASSIUM** are soluble in water, and afford no precipitates with pure or carbonated alkalis. They produce a precipitate in solution of chloride of platinum. They are not changed by sulphuretted hydrogen, nor by ferrocyanuret of potassium. Added to sulphate of alumina, they enable it to crystallize, so as to form alum. The solution



of potassa (and of most of its salts) is well characterized by the action of tartaric acid and of fluosilicic acid: a strong solution of tartaric acid added to a strong solution of potassa, causes no precipitate till the point of neutralization is exceeded; excess of the acid then produces a crystalline precipitate of *bitartrate of potassa*: when the solutions are dilute the precipitate is slowly formed and the crystals more apparent: the precipitate is dissolved by the addition of muriatic, nitric, sulphuric, or oxalic acid, but not by tartaric, or by acetic acid. Solutions of carbonated and caustic potassa, soda, and ammonia, dissolve the precipitate with ease; but the addition of a small quantity of a strong acid, reproduces it, and it is again dissolved by a greater quantity of the same acid. Fluosilicic acid produces a transparent gelatinous precipitate in solutions of potassa and of its salts, which is iridescent when it subsides, and dries into a white powder. Free muriatic acid renders it opalescent. An alcoholic solution of carbazotic acid produces a yellow crystalline precipitate in solutions of potassa and its salts. The neutral soluble salts of potassa may for the most part be heated to redness without suffering decomposition, especially if air be excluded; few of these are insoluble in water. In using the test of chloride of platinum to detect potash salts, the absence of ammoniacal salts must be previously ascertained, as they generally produce analogous effects upon that reagent.

## § II. SODIUM.

SODIUM, (Natrium of the German chemists,) discovered by Sir H. Davy in 1808, was obtained from soda, by an operation analogous to that for procuring potassium from potassa, by the gun-barrel; but the hydrate of soda is more difficult of decomposition than that of potassa, and the product of metal less certain and abundant: it may be facilitated, according to Thenard, by fusing the soda with a small proportion of potassa; so that an alloy of sodium and potassium distils over, which may be decomposed by keeping it in an open vessel in oil of turpentine; the potassium combines with the oil, and the sodium remains pure and metallic.

Sodium is soft, malleable, and easily sectile, and does not, like potassium, become brittle at  $32^{\circ}$ ; but even at that low temperature several globules may be welded together by pressure. Its specific gravity, according to Davy, is 0.9348; according to Gay Lussac and Thenard, it is 0.972 at  $59^{\circ}$ . In colour it resembles silver, but instantly tarnishes on exposure to air. It softens at about  $122^{\circ}$ : it fuses at about  $190^{\circ}$ , and is volatile at a white heat. It burns when heated in contact with air, and requires the same cautions to preserve it as potassium.

SODIUM AND OXYGEN: SODA. The affinity of sodium for oxygen appears to be less than that of potassium. When sodium is thrown upon water, it produces violent action, but the metal does not in general inflame, unless the quantity of water be very small; hydrogen is evolved, and a solution of soda is procured. By the quantity of hydrogen evolved, we learn that *protoxide of sodium*, or *soda*, ( $SO + O$ ) or S, consists of about 74.6 sodium, and 25.4 oxygen *per cent.*; and, if it be considered as the protoxide, the number representing the metal will be 24 (23.3 Gmelin and Turner), and anhydrous soda will consist of

Sodium . . .	1	..	24	..	75	..	Davy.
Oxygen . . .	1	..	8	..	25	..	74.6
	<hr/>		<hr/>		<hr/>		25.4
	1		32		100		100.0

PEROXIDE OF SODIUM, ( $SO + 1\frac{1}{2}O$ .) By heating sodium in oxygen, it burns vividly, and a yellowish-green *peroxide* is formed, which, by the action of water, evolves oxygen, (as is the case with peroxide of potassium,) and produces a solution of the protoxide. Peroxide of sodium is composed, according to Davy, of

Sodium . . .	1	..	24	..	66.7
Oxygen . . .	$1\frac{1}{2}$	..	12	..	33.3
	<hr/>		<hr/>		<hr/>
	1		36		100.0

*Anhydrous oxide of sodium* is obtained in the same way as anhydrous potassa, and resembles it in appearance, but is less fusible and less volatile.

HYDRATE OF SODA OR CAUSTIC SODA ( $S+q$ ) as it usually occurs in the laboratories, is obtained from the *carbonate*, by the action of lime and alcohol, as described under the head *Potassa*. Its colour is grayish-white; its specific gravity is 2.0 (Dalton); it requires a red heat for fusion; and when intensely heated upon charcoal, as by the oxygen or oxyhydrogen blowpipe, it evaporates and tinges the flame violet. It has the same general characters as hydrate of potassa: like it, it retains water at a red heat, and is deprived of it by the same means. It consists of

Soda . . .	1	..	32	..	78.1	..	Davy.
Water . . .	1	..	9	..	21.9	..	77.1
	<hr/>		<hr/>		<hr/>		22.9
	1		41		100.0		100.0

Like potassa, it may be obtained in crystals from its concentrated aqueous solution, containing a larger relative quantity of water.

The following Table by Dalton shows the proportion of anhydrous soda in solutions of different specific gravities:—

Specific gravity of solution.	Dry Soda per cent. by weight.	Boiling point.
1.85	63.6	600°
1.72	53.8	400
1.63	46.6	300
1.56	41.2	280
1.50	36.8	265
1.47	34.0	255
1.44	31.0	248
1.40	29.0	242
1.36	26.0	235
1.32	23.0	228
1.29	19.0	224
1.23	16.0	230
1.18	13.0	217
1.12	9.0	214
1.06	4.7	213

Soda is distinguished from potassa, by forming an *efflorescent* paste when exposed to the atmosphere: potassa, under the same circumstances, *deliquesces*. If excess of tartaric acid be added to a solution of soda,

there is no precipitation ; but in solution of potassa it occasions a deposit of a number of minute crystals. Solution of soda occasions no precipitate when added to solution of chloride of platinum. Solution of potassa occasions a yellow precipitate in solution of platinum. In combination with acids it produces a perfectly distinct class of salts, and its affinity for the acids is a little inferior to that of potassa.

CHLORIDE OF SODIUM. (*SO + C.*) Sodium, when heated in chlorine, burns vividly, and produces a white compound, of a pure saline flavour. It has all the properties of *common salt* or *muriate of soda*, and consists of

							Ure. 'v
Sodium . .	1	. .	24	. .	40	. .	39.98
Chlorine . .	1	. .	36	. .	60	. .	60.02
	1		60		100		100.00

Chloride of sodium is decomposed when heated with potassium: sodium and chloride of potassium are the results.

When hydrate of soda is heated in chlorine, oxygen and water are evolved, and chloride of sodium formed ; when heated in muriatic acid gas, the water of the hydrate is first expelled, and then the oxygen of the soda combines with the hydrogen of the muriatic acid to form water, and the sodium and chlorine unite to form the chloride.

Common salt exists abundantly in nature both as a solid fossil, and dissolved in spring water, and in the ocean. Extensive beds of it are found in Cheshire, where it is known under the name of *rock-salt*. From these sources the immense demands are supplied ; that is, either by evaporating brine-springs, or sea-water, or quarrying it from the mine.

When heated, chloride of sodium falls into pieces with a crackling noise, or *decrepitates*. At a red heat it fuses without undergoing any decomposition, and on cooling concretes into a hard white mass ; at a bright-red heat it slowly sublimes, and tinges flame of a beautiful blue colour. It is very nearly insoluble in absolute alcohol. In the solubility of common salt in water, there is this peculiarity, that it is taken up nearly in the same proportion by cold and by hot water ; so that, although its solution deposits crystals during evaporation, it does not do so by cooling. According to Berzelius, 1 part of salt dissolves in  $2\frac{1}{7}$  of water at  $60^\circ$ , and in  $2\frac{1}{7}$  of water at  $212^\circ$ . According to Gay Lussac, 100 parts of water at  $58^\circ$  dissolve 36 of salt ; at  $140^\circ$ , 37 parts ; and at  $225^\circ$ , which is the boiling-point of a saturated solution, 100 parts of water dissolve 40.38. At  $32^\circ$  water dissolves rather more than at  $60^\circ$ . When pure, chloride of sodium does not alter by exposure to air, though it is generally more or less deliquescent, from containing chlorides of magnesium and of calcium : obtained by slow or spontaneous evaporation, it crystallizes in solid cubes ; but when procured, as is usually the case, at a boiling heat, by removing its crystals from the surface of its solution whilst evaporating, it exhibits the form of a hollow quadrilateral pyramid. These crystals are all anhydrous, though they often include a little interstitial water. A concise account of the different methods of manufacturing salt will be found in Aikin's *Dictionary*, Art. MURIATE OF SODA. Dr. Henry states (*Phil. Trans.* 1810) that the various forms under which salt is known in commerce, such as *bay-salt*, *fishery-salt*, &c..

arise from modifications in the size and hardness of the grain, and not from any essential difference of composition. The following table includes his general results :—

1000 Parts by Weight consist of										
Kind of Salt.	Insoluble Matter.	Muriate of Lime.	Muriate of Magnesia.	Total Earthy Muriates.	Sulph. of Lime.	Sulph. of Magnesia.	Total Sulphates.	Total impurity	Pure Muriate of Soda.	
For. Bay Salt.	St. Ube's . . .	9	trace	3	3	23 $\frac{1}{2}$	4 $\frac{1}{2}$	23	40	960
	St. Martin's . .	12	do.	3 $\frac{1}{2}$	3 $\frac{1}{2}$	19	6	25	40 $\frac{1}{2}$	959 $\frac{1}{2}$
	Oleron . . . . .	10	do.	2	2	19 $\frac{1}{2}$	4 $\frac{1}{2}$	23 $\frac{3}{4}$	35 $\frac{3}{4}$	964 $\frac{1}{4}$
Brit. Salt fr. Sea-water.	Scotch (common)	4	—	28	28	15	17 $\frac{1}{2}$	32 $\frac{1}{2}$	64 $\frac{1}{2}$	935 $\frac{1}{2}$
	Scotch (Sunday) .	1	—	11 $\frac{1}{2}$	11 $\frac{1}{2}$	12	4 $\frac{1}{2}$	16 $\frac{1}{2}$	29	971
	Lymington (com.)	2	—	11	11	15	35	50	63	937
	Ditto (cat) . . .	1	—	5	5	1	5	6	12	988
Cheshire Salt.	Crushed rock . .	10	0. $\frac{1}{16}$	0. $\frac{3}{16}$	0. $\frac{1}{4}$	6 $\frac{1}{2}$	—	6 $\frac{1}{2}$	16 $\frac{3}{4}$	983 $\frac{1}{4}$
	Fishery . . . . .	1	0. $\frac{1}{4}$	0. $\frac{3}{4}$	1	11 $\frac{1}{4}$	—	11 $\frac{1}{4}$	13 $\frac{1}{4}$	986
	Common . . . . .	1	0. $\frac{1}{4}$	0. $\frac{3}{4}$	1	14 $\frac{1}{2}$	—	14 $\frac{1}{2}$	16 $\frac{1}{2}$	983 $\frac{1}{2}$
	Stoved . . . . .	1	0. $\frac{1}{4}$	0. $\frac{3}{4}$	1	15 $\frac{1}{2}$	—	15 $\frac{1}{2}$	17 $\frac{1}{2}$	982 $\frac{1}{2}$

Chloride of sodium is decomposed by moist carbonate of potassa, and chloride of potassium and carbonate of soda are the results. (Westrumb in English translation of *Crell's Journal*, ii., 127.) In the common process for obtaining muriatic acid it is decomposed by sulphuric acid. In this decomposition there is a transfer of the oxygen contained in the water of the sulphuric acid to the sodium of the salt, the chlorine of which combines with the hydrogen of the water to produce muriatic acid gas. The oxide of sodium unites with the dry sulphuric acid to produce *sulphate of soda*. It is also decomposed by nitric acid. When chloride of sodium and ferruginous clay are heated together, the silica and alumina of the clay are vitrified by the soda of the salt, and its chlorine combines with the iron; it is upon this principle that it is used as a glaze for stoneware, being thrown into the furnaces or ovens in which the articles are baked, it is volatilized and decomposed upon their surfaces.

Common salt is of most extensive use as a preservative of food, and as a condiment, as a source of soda and of muriatic acid and chlorine, and for various agricultural and horticultural purposes. (*Quarterly Journal*, x., 52.) Glauber first obtained muriatic acid from it, and the existence of soda in it was first shown by Duhamel.

CHLORIDE OF SODA OR CHLORITE OF SODA is formed by passing chlorine into a cold and dilute solution of caustic soda, or by decomposing chloride of lime by carbonate of soda, as suggested by M. Payen (*Quart. Jour. N.S.*, i., 236). It is powerfully bleaching and smells of chlorine: exposed to air it absorbs carbonic acid and evolves chlorine, hence it may be used as a disinfectant (see *carbonate of soda*). When heated, it undergoes changes similar to those produced by passing chlorine into a strong solution of soda, that is, chlorate of soda and chloride of sodium are formed.

CHLORATE OF SODA ( $S + C'$ ) was procured by Mr. Chenevix (*Phil. Trans.*, 1802,) by the same process as chlorate of potassa, but not possessing less solubility than chloride of sodium, the two substances are difficultly separable. Vanquelin obtained it by saturating chloric acid with soda. Its crystals resemble those of chlorate of potassa; its taste is also nearly similar. It dissolves in three parts of cold water, and in somewhat less at  $212^\circ$ . It is more soluble in alcohol than chloride of sodium; hence that solvent is sometimes used to separate the two compounds. It is slightly deliquescent in very damp weather.

SODIUM AND IODINE act upon each other with the same phenomena as potassium, and an *iodide of sodium* ( $SO + i$ ) is obtained. It may also be formed by adding iodine to a solution of caustic soda and evaporating to dryness (as for iodide of potassium). It is contained in the mother-liquor of kelp, in the ashes of burned sponge, &c., and in those cases is resorted to as a source of iodine, and is decomposed by sulphuric acid and oxide of manganese (see p. 340). The hydriodic acid and soda produce a deliquescent salt, which crystallizes in flat rhomboidal prisms; when heated it fuses, and loses its water of crystallization. The residue is iodide of sodium. When intensely heated it becomes slightly alkaline, and is volatilized. 100 parts of water at  $60^\circ$  dissolve 173 of this iodide. It is also soluble in alcohol.

IODATE OF SODA ( $SO + O$ ) + ( $i + 5O$ ) or ( $S + i'$ ) is made by dissolving iodine in solution of soda; a white compound forms, which is the iodate with a portion of iodide of sodium; the latter may be removed by alcohol, which does not dissolve the iodate. 100 parts of water at  $60^\circ$  dissolve 7.3 of this salt. It forms small prismatic tufted crystals, which, when heated, afford oxygen and iodide of sodium. (Gay Lussac, *Ann. de Chim.*, xci.)

SODIUM AND BROMINE act upon each other with much intensity, and the resulting *bromide of sodium* ( $SO + b$ ) is a fusible compound, soluble in water, and crystallizing at  $86^\circ$  in anhydrous cubes, but at lower temperatures in hexagonal tables, containing 26.37 per cent. of water. The *anhydrous bromide* consists of

Sodium	.	.	1	.	.	24	.	.	23.55
Bromine	.	.	1	.	.	78	.	.	76.45
			1			102			100.00

And the hexagonal *hydrate* of

Anhydrous bromide	.	.	1	.	.	102	.	.	Mitscherlich. 73.63
Water	.	.	4	.	.	36	.	.	26.37
			1			138			100.00

When bromine acts upon solution of soda, bromide of sodium and *bromate of soda* ( $S + bl$ ) are the results.

SODIUM AND FLUORINE: FLUORIDE OF SODIUM ( $SO + f$ ) is obtained by saturating hydrofluoric acid with soda, and evaporating to dryness; a white and difficultly-fusible compound results, the aqueous solution of which, when pure, furnishes cubical crystals, and acts upon glass. 100 parts of water dissolve 4 of this fluoride, and it is not more soluble in hot than in cold water. It may also be obtained by mixing 10 parts of

silico fluoride of sodium with 11.2 of dry carbonate of soda and sufficient water to form a thin paste, which, when boiled, evolves carbonic acid, and concretes. When cold, it must be powdered and boiled with more water as long as it effervesces; then filtered and evaporated (in silver, as it acts on glass) till it crystallizes; the crystals must be redissolved and again formed, in order to separate adhering silica. During the formation of the crystals by slow evaporation, they exhibit the same luminous appearance as sulphate of potassa. When they retain any carbonate of soda, they are octoëdral, but when pure, always cubic. They are insoluble in alcohol. Berzelius obtained a crystallizable compound of this salt with hydrofluoric acid. Fluoride of sodium consists of

Sodium . . .	1	.	.	24	.	.	57.2
Fluorine . . .	1	.	.	18	.	.	42.8
	<hr style="width: 50%; margin: 0 auto;"/>			<hr style="width: 50%; margin: 0 auto;"/>			<hr style="width: 50%; margin: 0 auto;"/>
	1			42			100.0

NITRATE OF SODA.  $(SO + O) + (N + 5O)$  or  $(S + N')$ . The *cubic nitre* of old writers. This salt crystallizes in rhombs (Brooke, *Ann. Phil.*, 2nd series, v., 452), soluble in 3 parts of water at  $60^\circ$ , and in less than its weight at  $212^\circ$ \*. It has a cool sharp flavour, and is somewhat deliquescent, and therefore unfit for the manufacture of gunpowder. Berzelius found a mixture of 5 nitrate of soda, 1 charcoal, and 1 sulphur, to burn three times more slowly than a similar mixture with nitrate of potassa: its flame is orange-coloured. It is often found in crude nitre, resulting partly from the decomposition of common salt. Large quantities of *native nitrate of soda* have been discovered in Peru, forming a stratum covered with clay and alluvium of many miles in extent, and it now forms a considerable article of trade. It may be employed in fireworks, and used as a substitute for nitre (it being cheaper) in the manufacture of nitric acid, of sulphuric acid, and other cases in which large quantities of nitre are consumed. It is too expensive as a source of soda. Nitrate of soda is anhydrous, and consists of

Soda . . . .	1	.	.	32	.	.	37.2	Wenzel. 37.5
Nitric acid . .	1	.	.	54	.	.	62.8	62.5
	<hr style="width: 50%; margin: 0 auto;"/>			<hr style="width: 50%; margin: 0 auto;"/>			<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	1			86			100.0	100.0

SODIUM AND AMMONIA. When sodium is heated in ammoniacal gas, hydrogen is disengaged, and an olive-coloured fusible substance formed, composed, according to Gay Lussac and Thenard, of 100 sodium + 11.7 nitrogen. No analogous substance can be obtained by heating potassium in pure nitrogen gas.

SODIUM AND SULPHUR. The account of the action of sulphur on

\* This is the usual statement in chemical works, but nitrate of soda is certainly more soluble. Berzelius says that one part dissolves in two of water at  $60^\circ$ , and Gay Lussac (*Cours de Chimie*, Paris, 1828) asserts that 100 parts of water at  $32^\circ$ , dissolve 73 parts; and at  $212^\circ$ , 173 parts.

Its solubility, as given upon the authority of Marx, (Thomson's *System*, ii., 448,) is as follows:—

100 of water at $32^\circ$	dissolve	80.
-	-	50 - 22.7
.	-	61 - 55.
-	-	246 - 218.5

So that according to this account, its solubility at  $32^\circ$  is more than three times greater than at  $50^\circ$ .

potassium and potassa, and of sulphuretted hydrogen upon solution of the alkali, applies generally to sodium and soda, and their corresponding compounds. Sodium and sulphur combine when gently heated, with vivid ignition, and form a *sulphuret of sodium* ( $SO + S$ ). And the same compound may be obtained by the decomposition of sulphate of soda by hydrogen or by charcoal. Sulphuret of sodium is composed of

Sodium	. .	1	. .	24	. .	60
Sulphur	. .	1	. .	16	. .	40
		1		40		100

BISULPHURET OF SODIUM ( $SO + 2S$ ) is similarly constituted to the corresponding compound of potassium.

A concentrated aqueous solution of sulphuret of sodium yields square prismatic crystals of *hydrosulphuret of soda*, which, when heated, fuse in their water of crystallization and leave a white anhydrous salt. The solution, exposed to air, rapidly absorbs oxygen, and becomes a hyposulphite.

The hydrosulphurets of soda derive some additional interest as being produced, upon the large scale, in the principal processes for obtaining soda by the decomposition of the sulphate of soda, as will presently be stated.

HYPOSULPHITE OF SODA ( $S + \underline{S}$ ) is formed as hyposulphite of potassa. It is crystallizable in transparent four-sided prisms, deliquescent, of an intensely bitter taste, and insoluble in alcohol. Its aqueous solution readily dissolves moist chloride of silver. When heated, it fuses, then dries, and afterwards takes fire.

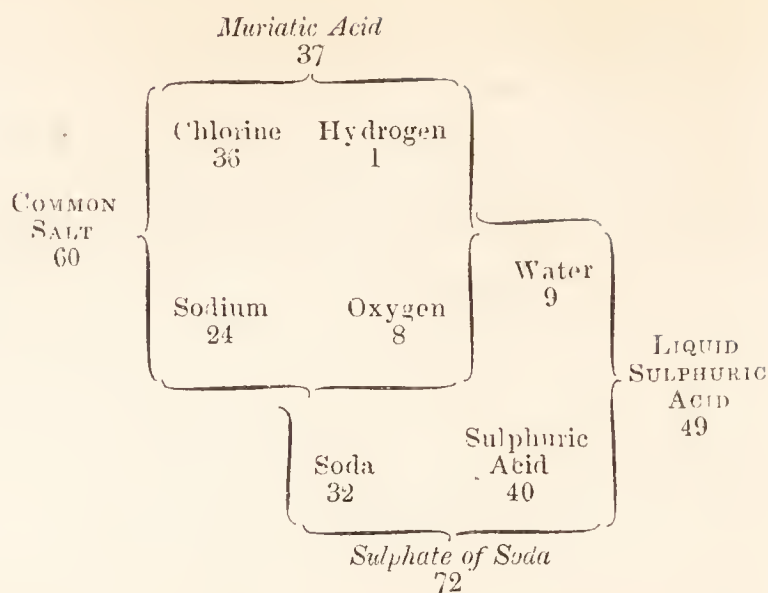
SULPHITE OF SODA ( $S + \underline{S}$ ) is crystallizable in transparent four and six-sided prisms, soluble in four parts of water at  $60^\circ$ . It consists of 32 soda + 32 sulphurous acid = 64. The crystals contain twelve proportionals of water = 108. There is also a crystallizable *bisulphite of soda*.

HYPOSULPHATE OF SODA ( $S + \underline{S}'$ ) may be obtained by decomposing hyposulphate of baryta by sulphate of soda: it forms transparent crystals of a peculiar bitterish taste, soluble in 2.1 of water at  $60^\circ$ , and in 1.1 at  $212^\circ$ . According to Heeren they contain

Soda	. . .	1	. .	32	. .	26.25
Hyposulphuric acid	. . .	1	. .	72	. .	58.85
Water	. . .	2	. .	18	. .	14.90
		1		122		100.00

SULPHATE OF SODA ( $S + S'$ ); GLAUBER'S SALT; SAL MIRABILE; is abundantly produced in the manufacture of muriatic acid, and of chlorine, by the action of sulphuric acid upon common salt (page 331). Common salt consists of 24 sodium + 36 chlorine. Sulphuric acid consists of 40 dry acid + 9 water. The water of the acid, consisting of 1 hydrogen + 8 oxygen, is decomposed. Its hydrogen is transferred to the chlorine to produce gaseous muriatic acid (1 hydrogen + 36 chlorine = 37 Mur. A.), and its oxygen unites to the sodium, forming dry soda (8 oxygen + 24 sodium = 32 soda). The 40 dry sulphuric acid unite to the 32 soda, to produce sulphate of soda, which will be represented by the number 72.

This decomposition is perhaps more clearly shown in the annexed diagram\* :—



Sulphate of soda is also a natural product, and occurs in many mineral waters; it may be formed by saturating dilute sulphuric acid with carbonate of soda, and evaporating the solution. It crystallizes from its aqueous solution in large prisms, transparent, and efflorescent when exposed to air. The primary crystal is an oblique rhombic prism. Exposed to dry air, the crystals part with between 50 and 60 per cent. of water.

The *anhydrous* salt, as above stated, is composed of

					Wenzel.			
Soda	.	1	..	32	..	44.5	..	44.3
Sulphuric acid	.	1	..	40	..	55.5	..	55.7
		1		72		100.0		100.0

And the ordinary crystals consist of

						Wenzel.		
Dry sulphate of soda	.	1	..	72	..	44.4	..	44.8
Water	.	10	..	90	..	55.6	..	55.2
		1		162		100.0		100.0

The taste of sulphate of soda is saline and somewhat bitter: it is soluble in rather less than three times its weight of water at 60°, and insoluble in alcohol. The solubility of sulphate of soda in water follows a singular law, first observed by Gay Lussac. (*Ann. de Chim. et Phys.*, xi.) After having increased rapidly to about the temperature of 92°, where it is at its maximum, it diminishes to 215°, and at that temperature the salt is nearly of the same solubility as at 87°.

At 32° 100 parts of water dissolve about 5. of anhydrous and 12. of crystallized salt.

50	-	-	-	-	10.	-	-	-	26.
60	-	-	-	-	11.	-	-	-	31.
70	-	-	-	-	16.	-	-	-	48.
77	-	-	-	-	28.	-	-	-	99.
87	-	-	-	-	43.	-	-	-	215.
92	-	-	-	-	50.	-	-	-	322.
104	-	-	-	-	48.	-	-	-	291.
122	-	-	-	-	46.	-	-	-	262.

\* The original substances are printed in capitals, the products in italics, and the components in common type.



When sulphate of soda is dissolved in its weight of boiling water, and a flask filled with it and tightly corked up, no crystallization generally ensues; but upon opening the flask it either immediately crystallizes, or does so upon touching the solution with a solid body. This experiment has already been referred to (p. 112). It sometimes, however, happens that a portion of the salt does crystallize, forming quadrangular crystals, which become opaque on exposure, and which, for sulphate of soda, are peculiarly hard; Mr. Faraday found these composed of

Dry sulphate of soda	.	1	..	72	..	50
Water	.	.	.	8	..	72
		1		144		100

If a solution of sulphate of soda, saturated at 91.5°, is evaporated at a higher temperature, opaque prisms of *anhydrous sulphate of soda* are deposited, the primary form of which is a rhombic octoëdron. Its specific gravity in this state is 2.462. (Haidinger.)

When exposed to heat, sulphate of soda undergoes watery fusion; that is, it melts in its water of crystallization, and a portion of anhydrous salt is deposited: when the water has evaporated, the residue may be raised to a high heat, without undergoing decomposition. At a red-heat it fuses. The salt which has been deprived of its water by heat has an acrid taste, and produces a sense of heat upon the tongue in consequence of its absorbing water, which it does with great avidity.

Gay Lussac obtained a powerful pyrophorus, by igniting a mixture of lamp-black and dry sulphate of soda, analogous to that mentioned under *Sulphate of Potassa*. (*Quarterly Journal*, iv., 208.)

Sulphate of soda is sometimes decomposed for the purpose of obtaining soda, by igniting it with chalk and charcoal, or with iron and charcoal, and various economical means have been proposed for obtaining sulphate of soda for the purpose: such as calcining a mixture of common salt, sulphate of lime, and charcoal; or a mixture of common salt and green vitriol; or by roasting, in a proper furnace, 100 parts of finely-powdered pyrites (bisulphuret of iron) with 40 of common salt, for sixty hours, and lixiviating the brownish-red mass which results, and from which about 45 parts of crystals of sulphate of soda are obtained. The addition of carbonaceous matter accelerates the process and increases the product. The manufacturers of bleaching-powder furnish large supplies of sulphate of soda. (See CHLORIDE OF LIME.) It is also made expressly for the production of soda, by the action of sulphuric acid upon chloride of sodium, the evolved muriatic acid being suffered to go to waste. But in whatever way the sulphate of soda is obtained, the following are the processes for its decomposition. (See Aikin's *Dictionary*—Art. MURIATE OF SODA.)

1. DECOMPOSITION OF SULPHATE OF SODA BY THE COMBINED ACTION OF CHALK AND CHARCOAL.—Take 1000 lbs. of calcined sulphate of soda, and 550 lbs. of charcoal, and mix the two ingredients accurately together by grinding; when the mixture appears complete, add by degrees 1000 lbs. of washed chalk, and continue the grinding till this also is mixed with the other materials. Now let a reverberatory furnace be lighted, and as soon

as it is red-hot, let it be charged with 400 or 500 lbs. (more or less, according to the size of the furnace,) of the above mixture, and close the door. During the first part of the process, while the materials are yet pulverulent, the flame must be kept as gentle as possible, lest it should carry part of the powder up the chimney; but as soon as the matter begins to clot, the flame may be increased. At this time the mass must be carefully worked about with an iron rake, in order to expose fresh surfaces to the action of the flame. When the whole has acquired a pasty consistence, jets of inflamed sulphuretted hydrogen will be perceived to issue from every part, accompanied by a moderate but very perceptible explosion and effervescence; and during the whole of this stage of the process the rake must be used very vigorously, in order to expedite the disengagement of the gas. When the jets of flame cease, and the matter becomes nearly fluid, the rake may be withdrawn, and a bar of cold iron is to be introduced from time to time, in order to judge of the progress of the operation by the sample that adheres to the end of it: if this cracks as it grows cold, and presents an uniform granular texture, the heat has been continued long enough, and the matter must then be speedily withdrawn, lest it should be fretted by the further action of the fire. The flame being accordingly turned off for a few minutes, the mass returns to a pasty consistence, and is withdrawn from the furnace by means of the rake. As soon as it becomes solid by cooling, it is to be broken into moderate-sized pieces, and kept for some days in a damp cellar, where it imbibes a considerable quantity of water and carbonic acid, falls to powder, and at the same time parts almost entirely with the sulphuretted hydrogen, to which its hepatic smell and flavour, when recent, are owing. It may now be brought to market, without any further preparation; or the alkaline part may be extracted and sold separately.

In order to separate the alkaline from the earthy part, lixiviation with cold water must be had recourse to: the clear liquor by evaporation to a pellicle, and subsequent cooling, deposits crystals of carbonated soda; and the mother-water, consisting chiefly of semicaustic soda, must be boiled down to dryness, and afterwards calcined till it is as white as pearlsh, in which state it is well fitted for the glass-makers.

500 lbs. of raw materials treated as above described, afford 276 lbs. of rough soda, of which 100 lbs. yield by lixiviation 37 lbs. 8 oz. of crystallized carbonate and 23 lbs. 2 oz. of dry semicaustic soda, with a small admixture of sulphuret of lime, and of other salts accidentally contained in the original sulphate.

## 2. DECOMPOSITION OF SULPHATE OF SODA BY MEANS OF IRON AND CHARCOAL.

Take	200 lbs.	calcined sulphate of soda.
	40	powdered charcoal.
	65	clippings of iron plate or old iron.
	22	charcoal, in the state of small coal.

---

327 lbs.

Having mixed the sulphate of soda with the powdered charcoal, let it be introduced into the reverberatory furnace, and treated for the first hour exactly as described in the foregoing process; then bring the mixture to complete fusion, and add 40 lbs. of the clippings, stirring the

materials well at the same time with an iron rake, in order to mix them more completely. In a short time after, the matter, which was at first quite fluid, will become pasty, accompanied with much foaming and boiling, till the clippings are dissolved. As soon as this takes place, 16 lbs. of small coal must be stirred in, which will immediately excite the disengagement of sulphuretted hydrogen mentioned in the former process. When this appearance begins to slacken, the remaining 25 lbs. of clippings and 6 lbs. of small coal are to be added in succession, and the stirring is to be diligently continued till the jets of inflamed gas almost cease. When this happens, the matter still fluid is to be run into moulds of sand, where it solidifies.

The rough soda thus prepared weighs 215 lbs., is of a blackish-brown colour, which becomes still darker by the contact of the air: when broken it has a kind of metallic lustre, and a close striated texture. To the taste it is caustic and hepatic. By exposure to a moist atmosphere it becomes covered with a yellow efflorescence, and quickly falls to powder, with a considerable disengagement of heat and sulphuretted hydrogen; at the same time it absorbs carbonic acid and water, so as to increase in weight, by an exposure of about twenty days, in the proportion of 5 to 8.

From the 215 lbs. of rough soda thus obtained, and increased by absorption of air and moisture to 344 lbs., may be obtained, by lixiviation and crystallization, 152 lbs. of carbonated soda; and the uncrystallizable mother-water will afford by evaporation about 47 lbs. of semicaustic soda, mixed with a little charcoal, sulphuret of iron, and other impurities. The insoluble residue weighs about 185 lbs., and is sulphuret of iron, with a little charcoal, in a state highly favourable for vitriolization. (See also Dumas' *Chimie appliquée aux Arts*.)

BISULPHATE OF SODA ( $S + 2 S'$ ) is obtained by adding sulphuric acid to a hot solution of sulphate of soda. It crystallizes in rhombic prisms, soluble in twice their weight of water at  $60^\circ$ , and containing water of crystallization. (LINK, Crell's *Annals*, 1796.) When a crystal of bisulphate of soda is held in the candle, it melts like ice. This salt liquefies at  $300^\circ$ , and may be kept at that temperature without much loss of weight. Its specific gravity is 1.8 at  $60^\circ$ . 100 of water dissolves 92.72 of this salt, so that it is more than twice as soluble as sulphate of soda. Its taste is very acid. (Thomson, *Ann. Phil.*, x., 439, 2nd series.) An *anhydrous bisulphate of soda* may be obtained by gently heating together in a platinum crucible 10 parts of dry sulphate of soda and 7 of sulphuric acid (specific gravity 1.85); the water of the acid escapes, and the residue may then be fused: it furnishes a very soluble but not a deliquescent salt, which, when distilled at a high temperature, affords *anhydrous sulphuric acid*. Anhydrous bisulphate of soda consists of

Soda . . . . .	1	..	32	..	28.55
Sulphuric acid . . . . .	2	..	80	..	71.45
	<hr/>		<hr/>		<hr/>
	1		112		100.00

The crystallized bisulphate of soda contains

Soda . . . . .	1	..	32	..	21.62
Sulphuric acid . . . . .	2	..	80	..	54.03
Water . . . . .	4	..	36	..	24.35
	<hr/>		<hr/>		<hr/>
	1		148		100.00

SESQUISULPHATE OF SODA. ( $S + 1\frac{1}{2}S'$ .) According to Thomson (*Ann. of Phil.*, 2nd. series, x. 436,) this salt is obtained when the residue after the decomposition of common salt by sulphuric acid in excess is dissolved in hot-water and set aside; it usually forms the first crop of crystals; they are transparent prisms, firmer and harder than the common sulphate, of an acid taste, but neither deliquescent nor efflorescent. Their specific gravity is 2.226, at  $63^\circ$ . 100 of water dissolve 25 of this salt. When water saturated with it is set aside, crystals of the common sulphate are formed: it loses but little weight even at a red-heat: it is anhydrous and consists of

Soda . . .	1	..	32	..	34.68
Sulphuric acid . . .	$1\frac{1}{2}$	..	60	..	65.32
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		92		100.00

AMMONIO-SULPHATE OF SODA ( $S + A + 2S'$ .) is a double salt, formed by saturating the bisulphate with ammonia, (LINK, *Crell's Annals*, 1796, i.) or, by dissolving the two sulphates in atomic proportions and crystallizing: it yields transparent prisms with rhombic bases, of a bitter taste. It consists of

Sulphate of Soda . . .	1	..	72	..	39.25
Sulphate of Ammonia . . .	1	..	57	..	31.18
Water . . .	6	.	54	..	29.57
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		183		100.00

SODIUM AND SELENIUM. The seleniuret of sodium has not been examined. *Selenite of soda* is very soluble and difficultly crystallizable. It tastes like borax. It is insoluble in alcohol, and not deliquescent. *Biselenite of soda* is also very soluble: its solution when evaporated to the consistence of syrup forms clusters of radiated crystals. At a red-heat it fuses and gives off acid so as to become neutral. *Quadri-selenite of soda* yields radiated crystals by spontaneous evaporation. (Berzelius.) *Seleniate of soda* may be obtained by detonating a mixture of selenium and nitrate of soda. It is isomorphous with sulphate of soda.

PHOSPHURET OF SODIUM ( $SO + p$ ) possesses the general properties of the corresponding compound of potassium.

HYPOPHOSPHITE OF SODA ( $S + \bar{p}$ ) is very soluble both in alcohol and water. (*Ann. de Chim et Phys.* ii. 142.) It may be obtained by mixing hypophosphite of lime with a slight excess of carbonate of soda, filtering, evaporating to dryness, and digesting in alcohol, which dissolves the hypophosphite, and which by very careful evaporation may be obtained in prismatic crystals.

PHOSPHITE OF SODA ( $S + \bar{p}$ ) forms rhombic crystals, very soluble in water and alcohol. (Dulong.)

SODA AND PHOSPHORIC ACID. There is considerable difference of opinion as to the number and composition of the *phosphates of soda*. The salt commonly termed *phosphate of soda*, or *rhombic phosphate*, (the *sal perlatum* of some old writers) is obtained by saturating the impure phosphoric acid, prepared from calcined bones by sulphuric acid (see *Phosphorus*), with carbonate of soda: the liquor is filtered, evaporated, and set aside to crystallize. The crystals form most readily in an alkaline solution: they are

oblique rhombic prisms, (Brooke, *Ann. of Phil.*, 2nd series, vi. 286,) always alkaline to test paper, efflorescent, and soluble in about 4 parts of cold and 2 of hot-water. This salt has a slightly saline and alkaline flavour, and has been used in medicine as an aperient under the name of *tasteless purging salt*. Its concentrated aqueous solution often deposits silky crystals, but they are of the same composition as the other form. The crystals when heated, fuse in their water of crystallization, and the salt afterwards runs into a clear glass, which becomes opaque on cooling: in this state it has the peculiarities of a *pyrophosphate*. Dr. Turner, upon the authority of Mr. Graham, (*Phil. Trans.*, 1833,) calls this salt *Triphosphate of soda with basic water*, but the analyses of Berzelius and Mitscherlich, represent it, in its anhydrous state, as composed of

				Berzelius.		Mitscherlich	
Soda	. . . 1	. . . 32	. . . 47	. . . 46.52	. . . 47.37		
Phosphoric acid	1	. . . 36	. . . 53	. . . 53.48	. . . 52.63		
	1	68	100	100.00	100.00		

And in its ordinary crystalline form, as containing

				Berzelius.	
Soda	. . . 1	. . . 32	. . . 18.2	. . . 17.67	
Phosphoric acid	. . . 1	. . . 36	. . . 20.5	. . . 20.33	
Water	. . . 12	. . . 108	. . . 61.3	. . . 62.00	
	1	176	100.0	100.00	

When a solution of this phosphate is evaporated at a temperature of 90°, it crystallizes according to Mr. Clarke, (*Brewster's Journal*, vii., 311,) in a modified form with only 8 atoms of water.

**PYROPHOSPHATE OF SODA.** When the above phosphate of soda is heated to redness, so as to expel its water, and again dissolved and crystallized, it acquires a new crystalline form (*Haidinger, Brewster's Journal*, vii., 314), and now, instead of precipitating nitrate of silver yellow, as the former salt does, it throws it down white, the former being a subphosphate, the latter, a neutral phosphate of that metal. (See pyrophosphoric acid, p. 445.) According to Clarke, it consists in this state of 1 atom of anhydrous phosphate and 10 atoms of water.

**BIPHOSPHATE OF SODA.** When phosphoric acid is added to a solution of rhombic phosphate of soda till it ceases to precipitate chloride of barium, it yields on evaporation, very soluble crystals of an acid taste. They are generally in the form of right rhombic prisms, but sometimes in rectangular octoëdra. They consist of

Soda	. . . 1	. . . 32	. . . 22.85
Phosphoric acid	. . . 2	. . . 72	. . . 51.40
Water	. . . 4	. . . 36	. . . 25.75
	1	140	100.00

**AMMONIO-PHOSPHATE OF SODA** exists in human urine, whence it was procured by the early chemists under the names of *microcosmic* and *fusible salt*. It may be formed by dissolving 5 parts of crystallized phosphate of soda with 2 of crystallized phosphate of ammonia, and evaporating. It forms transparent prismatic crystals, which are very fusible, and at a red-heat lose water and ammonia, and leave biphosphate of soda, in the form of a transparent glass. They consist, according to Mitscherlich, of

Soda . . . . .	1	..	32	..	15.2
Ammonia . . . . .	1	..	17	..	8.0
Phosphoric acid . . . . .	2	..	72	..	34.1
Water . . . . .	10	..	90	..	42.7
	<hr/>		<hr/>		<hr/>
	1		211		100.0

POTASSO-PHOSPHATE OF SODA is obtained by saturating the excess of acid in the biphosphate of potassa, with soda. It forms prismatic crystals, composed, according to Mitscherlich, of

Soda . . . . .	1	..	32	..	10.50
Potassa . . . . .	1	..	48	..	15.75
Phosphoric acid . . . . .	2	..	72	..	23.60
Water . . . . .	17	..	153	..	50.15
	<hr/>		<hr/>		<hr/>
	1		305		100.00

CARBONATE OF SODA (S + CAR'.) This important salt is largely obtained by the combustion of marine plants, the ashes of which afford, by lixiviation, the impure alkali called *soda*. Two kinds of rough soda occur in the market, *barilla* and *kelp*; besides which, some *native carbonate of soda* is also imported. Barilla is the semifused ash of the *salsola soda*, which is largely cultivated upon the Mediterranean shore of Spain, in the vicinity of Alicant\*. Kelp consists of the ashes of sea-weeds, which are collected upon many of the rocky coasts of Britain, and burned in kilns, or merely in excavations made in the ground, and surrounded by stones. It seldom contains more than five per cent. of carbonated alkali, and about 24 tons of sea-weed are required to produce one ton of kelp. The best produce is from the hardest *fuci*, such as the *serratus*, *digitatus*, *nodosus*, and *vesiculosus*. (Macculloch's *Western Islands*, vol. i., p. 122.) The rough alkali is contaminated by chlorides of potassium and sodium, and by other impurities, from which it may, to a certain extent, be separated by solution in a small portion of water, filtrating the solution, and evaporating it at a low heat. At present the British market is chiefly supplied with carbonate of soda, obtained by the decomposition of sulphate of soda, by processes similar to those above mentioned (p. 579): it is manufactured to an enormous extent, at a very cheap rate, and of extreme purity; in many of the arts it has accordingly been substituted for potash. Small quantities of carbonate of soda are often found in an efflorescent form, upon walls containing lime and common salt. It is found in some mineral waters. A very pure carbonate of soda may be obtained by calcining acetate of soda at a red heat, and lixiviating the residue.

The primitive crystalline form of carbonate of soda is an oblique rhombic prism, the modifications of which have been described by Mr. Brooke, (*Ann. of Phil.*, N. S., vi., 287.) Its sp. gr. is 1.62. It is soluble in twice its weight of water at 60°, and in less than its own weight at 212°. "The strongest solution that can be preserved at the temperature of the atmosphere has the specific gravity 1.26; but even this is liable to partial crystallization." (HENRY.) Its taste is strongly alkaline, and it greens vegetable blues. It fuses very readily in its water

\* Respecting the sources and preparation of this carbonate, see *Ann. de Chim.*, xlix., 267.

of crystallization, and on pouring off the fused salt, a portion of anhydrous carbonate remains. The fused salt congeals at about  $90^{\circ}$ . Exposed to a dry atmosphere the crystals effloresce, and gradually erumble down into a white powder: at a red-heat it loses the whole of its water. It is the *Subcarbonate of Soda* of the *London Pharmacopæia*.

In its anhydrous state it consists of

					Berzelius.	Dalton.			
Soda . . . . .	1	..	32	..	59.25	..	58.75	..	59.6
Carbonic acid	1	..	22	..	40.75	..	41.25	..	40.4
	<u>1</u>		<u>54</u>		<u>100.00</u>		<u>100.00</u>		<u>100.0</u>

The perfect crystals, as they ordinarily occur, consist of

					Bergman.		
Soda . . . . .	1	..	32	..	22.25	..	20
Carbonic acid . . . . .	1	..	22	..	15.25	..	16
Water . . . . .	10	..	90	..	62.50	..	64
	<u>1</u>		<u>144</u>		<u>100.00</u>		<u>100</u>

When the crystals are formed at a temperature between  $80^{\circ}$  and  $90^{\circ}$ , they sometimes form large right rectangular prisms, terminated by a four-sided pyramid: these only contain 8 equivalents of water. A saturated solution of carbonate of soda, kept for a long time at  $120^{\circ}$ , deposited transparent prismatic crystals, harder than the common carbonate, and containing only 1 equivalent of water; and another variety, described by Mohs contained  $1\frac{1}{2}$  of water.

In the analysis of barilla, kelp, and other impure kinds of soda, to ascertain the relative proportion of soda, it may be useful to know that 100 parts of dilute nitric acid, specific gravity 1.36, will saturate 50 parts of dry carbonate of soda, which are equivalent to about 29 of pure soda; or 460 grains of dilute sulphuric acid, specific gravity 1.141, neutralize 100 grains of the dry carbonate. From either of these data, the quantity of real alkali in any sample of the rough salt may easily be calculated. But the method of ascertaining the proportion of soda, or of carbonate of soda, in these cases, by means of the *alkalimeter*, has already been described. (See *Carbonate of Potassa*, p. 563.)

LABARRAQUE'S SODA DISINFECTING LIQUID. It has already been stated that, when excess of chlorine is passed into a solution of carbonate of potassa or of soda, carbonic acid is expelled, and chlorides and chlorates formed: by peculiar management, however, chlorine may be combined with a solution of carbonate of soda, and the resulting combination has, from the uses made of it, and the name of its inventor, been termed as above. It is obtained as follows: 2800 grains of crystallized carbonate of soda are dissolved in 1.28 pints of water, and being put into a Woulfe's apparatus, the chlorine slowly evolved from a mixture of 967 grains of salt with 750 grains of black oxide of manganese, and 967 grains of sulphuric acid, previously diluted with 750 grains of water, is carefully passed into it. No carbonic acid is evolved, and a pale yellow liquid is the result; its taste is sharp, saline, and astringent, and it at first reddens, and then bleaches turmeric paper. It is but little changed by a boiling heat, and gives out no chlorine. By *careful* evaporation, it furnishes crystals which produce the original liquid when redissolved; but exposed to the air, and suffered to evaporate spontane-

ously, the chlorine escapes, and crystals of carbonate of soda are obtained. (Faraday, *Quarterly Journal, N. S.*, vol. ii., p. 84.)

BICARBONATE OF SODA ( $S + 2 CAR'$ ), is formed by passing carbonic acid through a strong solution of the carbonate. Small crystals are deposited, which, when very carefully dried at common temperatures, consist of 1 atom of bicarbonate of soda, with, according to some, 1 atom, according to others, 2 atoms, of water. Both combinations may probably be formed.

The bicarbonate of soda has a very slightly alkaline taste, and it is much less soluble in water than the carbonate; requiring, according to Berthollet, 8, according to Rose, 13 of cold water. It loses carbonic acid if moistened and left in the vacuum of an air-pump, and the gas is also evolved when one part of the salt is boiled with four of water. In these cases the salt appears to be converted into a *sesqui-carbonate*. (*Quarterly Journal*, xv. 383.) At a red-heat, bicarbonate of soda loses its water, and half its acid, and becomes converted into dry carbonate of soda.

This salt, as well as the bicarbonate of potassa, may be obtained by treating their respective carbonates with carbonate of ammonia; pure ammonia is evolved and bicarbonates are formed. Bicarbonate of soda may also be obtained by condensing carbonic acid upon crystals of the carbonate; a portion of the water of the latter salt separates, and when the gas ceases to be absorbed, it is found converted into a porous and friable bicarbonate, which must be carefully dried at a low temperature, otherwise it loses a portion of its carbonic acid, and becomes a sesqui-carbonate.

In the manufacture of this bicarbonate for the purpose of commerce, 160 lbs. of carbonate may be dissolved in 13 gallons of water, and carbonic acid thrown into the solution in a proper apparatus. The bicarbonate falls as it forms to the amount of about 50 lbs., and being separated from the solution may be conveniently dried by pressure in an hydraulic press, and subsequent exposure to heat not exceeding  $100^{\circ}$ . A fresh portion of carbonate is dissolved in the mother-liquor, and the operation repeated as before.

SESQUICARBONATE OF SODA. ( $S + 1\frac{1}{2} CAR'$ .) A carbonate of soda occurs *native* in the Soda Lakes of Hungary, and in abundance in Africa, in the province of Gahena, near Fezzan. The natives call it *Trona*. It is crystallized in hard striated masses, and is not altered by exposure to air: indeed, the walls of Cassar, a fort now in ruins, are said to have been built of it. Mr. R. Phillips has shown that it is a compound intermediate between the carbonate and bicarbonate, (*Quarterly Journal*, vii. 298,) consisting of

						Klaproth*.		Phillips
						<i>Trona</i> .		
Soda . . . .	1	..	32	..	38.6	..	37.0	} . . . 78.2
Carbonic acid	$1\frac{1}{2}$	..	33	..	39.7	..	38.0	
Water . . . .	2	..	18	..	21.7	..	22.5	
	<hr/>		<hr/>		<hr/>		<hr/>	<hr/>
	1		83		100.0		97.5	100.0
Sulphate of soda	.	.	.	.	.	.	2.8	
							<hr/>	
							100.0	

\* *Beiträge*, vol. iii. p. 83.



A very productive soda-lake also exists in South America, in Maracaybo, one of the provinces of Venezuela. (*Quarterly Journal*, i., 188.)

SODIUM AND CYANOGEN act with the same phenomena as potassium, and the *hydrocyanate of soda* is obtained in the same way, or by decomposing hydrocyanate of lime by carbonate of soda. *Cyanate of soda* is a crystallizable salt. (Wöhler.) *Sulphocyanuret of sodium* and *sulphocyanate of soda*, are formed as the corresponding salts of potassa; the latter forms deliquescent rhombic crystals.

BORATE OF SODA; BORAX. (S + *bor'*.) This salt, which has been very long known, is imported from India in an impure state, and covered by a soapy matter, under the name of *Tincal*, *Pounxa*, or *Chrysocolla*, which, when purified, is called *Borax*. It has also lately been manufactured by combining soda with native boracic acid, imported from the South of Italy. It crystallizes in irregular hexaëdral prisms, slightly efflorescent. Its taste is alkaline and styptic, and it has an alkaline reaction upon colours. It is soluble, according to Wallerius, in 20 parts of water at 60°, and in 6 parts of boiling water; or, according to Berzelius, in 12 of cold and 2 of hot water, proportions which I believe more correct. When heated it loses water of crystallization, and becomes a porous friable mass, called *calcined borax*. At a red-heat it runs into a transparent glass, which, by exposure to air, becomes opaque and pulverulent upon the surface.

Anhydrous borax consists of

Soda . . .	1	..	32	..	31.4
Boracic acid	1	..	68	..	68.6
	1		100		100.0

and crystallized borax, of

Soda . . .	1	..	32	..	16.85	..	17
Boracic acid .	1	..	68	..	35.80	..	34
Water . . .	10	..	90	..	47.35	..	49
	1		190		100.00		100

Sulphuric acid decomposes this salt, producing sulphate of soda and boracic acid (see p. 510.) It is also decomposed by nitric and muriatic acids, and by the greater number of the vegetable acids. It has a place in the *Pharmacopœia*. It is often used as a blowpipe flux. Muslin and other articles of clothing may be rendered, to a certain extent, incombustible, by steeping them in a solution of borax: when dry, they cannot readily be inflamed.

BOROFLUORIDE OF SODIUM is obtained by combining fluoride of sodium with fluoboric acid: it forms prismatic crystals of a bitter and sour taste, easily soluble in water, fusible and anhydrous. (Berzelius.)

SODIUM AND POTASSIUM form an *alloy*, which, if composed of one part of potassium and three of sodium, remains fluid at 32°. Equal parts of the metals form a brittle crystallizable alloy.

THE SALTS OF SODIUM are soluble in water. They are not precipitated either by pure or carbonated alkalis, or hydrosulphuret of ammonia, or tartaric acid, or ferro-cyanuret of potassium; they produce no precipitate in solution of chloride of platinum, and do not convert sulphate of alumina into distinctly octoëdral alum.

## § III. LITHIUM.

IN the analysis of a mineral found in the mines of Utö, in Sweden, in the year 1808 (*Ann de Chim. et Phys.*, x.), called *petalite*, M. Arfwedson discovered between 5 and 6 *per cent.* of an alkaline substance, which was at first supposed to be soda; but, finding that it required for its neutralization a much larger quantity of acid than soda, he was led to doubt its identity with that alkali, and the further prosecution of his inquiries fully demonstrated that it possessed peculiar properties. The mineral called *triphane*, or *spodumene*, also affords the same substance, to the amount of nearly 9 *per cent.*, and it exists in *lepidolite* and in several varieties of *mica*, and, according to Berzelius, in the waters of Carlsbad, in Bohemia: the term *lithia*, deduced from its lapideous original ( $\lambda\iota\theta\epsilon\iota\omicron\varsigma$ , *lapideus*), has been applied to it.

The following is Arfwedson's mode of obtaining lithia from the *Petalite*: Reduce the mineral to a fine powder, and fuse it with about half its weight of potassa; dissolve the fused mass in muriatic acid, filter, and evaporate to dryness; digest the dry mass in alcohol; the only substance present, soluble in that liquid, is the *chloride of lithium*, which is taken up, and by a second solution and evaporation is obtained pure. It may be decomposed by digesting carbonate of silver in its aqueous solution, by which a carbonate of lithia is formed, decomposable by lime, in the way of the other alkaline carbonates.

Berzelius separates lithia from *spodumene* or from *pétalite* as follows: One part of the mineral is reduced to a fine powder with about two parts of fluor-spar; this mixture is made into a thin paste with sulphuric acid, and heated in a silver crucible as long as acid vapours are given off, and ultimately to redness nearly: the dry mass is then digested in water, filtered, boiled with caustic ammonia to precipitate any alumina that may be present, filtered again, and evaporated to dryness: the dry mass, after having been heated to redness, to expel sulphate of ammonia, is pure *sulphate of lithia*, from the solution of which the lithia may be thrown down in the state of *carbonate*, by carbonate of ammonia.

LITHIA, OR PROTOXIDE OF LITHIUM ( $li + o$ ), is a white caustic substance, and when submitted, in the state of hydrate, to the action of the Voltaic pile, it is decomposed with the same phenomena as potassa and soda; a brilliant white and highly combustible metallic substance is separated at the negative pole. The properties of this metal have not hitherto been investigated, in consequence of the difficulty of procuring any quantity of its oxide.

Pure lithia is not very soluble in water; its solution tastes acrid like the other fixed alkalis. It acts powerfully on vegetable blues, converting them to green. It is very sparingly soluble in alcohol. It does not deliquesce by exposure, but absorbs carbonic acid and becomes opaque: it affords no precipitate with chloride of platinum, in which it differs from potassa, but resembles soda. It attacks platinum in its pure and carbonated state, and hence must be fused in a silver crucible. When its salts are heated on platinum before the blow-pipe, they tinge the flame red. Its principal distinctive characters are found in its salts.

Obtained by evaporating its aqueous solution, lithia is in the state of *hydrate*, the composition of which has not been ascertained: it melts at a red-heat, retaining water.

Direct experiments upon the composition of lithia are yet wanting. By calculation from the composition of the sulphate, as analyzed by Vauquelin, it would appear to contain about 55.2 lithium + 44.8 oxygen; by other experimentalists, nearly the same results have been admitted; so that the number 10 has been generally assumed as the equivalent of lithium; but from the analysis of some of its salts by M. Hermann, of Moscow (Poggend. xv.), as also by C. Gmelin, it appears that its atomic weight does not exceed 8; or even according to Hermann, 6. So that, taking Gmelin's results as the mean, lithia will consist of

Lithium	.	.	1	..	8	..	50
Oxygen	.	.	1	..	8	..	50
			<u>1</u>		<u>16</u>		<u>100</u>

CHLORIDE OF LITHIUM. (*li+c.*) This compound is obtained by dissolving lithia or its carbonate in muriatic acid, evaporating the solution to dryness, and fusing it out of the contact of air: it is a white semi-transparent substance. It evidently differs from the chlorides of potassium and sodium, in being extremely deliquescent; in being soluble in alcohol; in being decomposed when strongly heated in the open air, when it loses chlorine, absorbs oxygen, and becomes highly alkaline; in being very difficultly crystallizable in cubes; and in tinging the flame of alcohol of a red colour. It probably consists of

					Hermann	Gmelin.				
Lithium	.	1	..	8	..	18.25	..	14.66	..	18.43
Chlorine	.	1	..	36	..	81.75	..	85.34	..	81.57
		<u>1</u>		<u>44</u>		<u>100.00</u>		<u>100.00</u>		<u>100.00</u>

IODIDE OF LITHIUM. The action of *iodine*, of *hydriodic acid*, and of *iodic acid*, on lithia, has not been examined, nor have its compounds with *bromine* been investigated.

FLUORIDE OF LITHIUM is very difficultly soluble. Its solution deposits small opaque crystals. (Berzelius.)

NITRATE OF LITHIA (*L+n'*) is a very soluble deliquescent salt, fusible and decomposed by heat; its taste is cooling; it crystallizes in rhombic prisms; and is soluble in alcohol.

SULPHURET OF LITHIUM. The action of sulphur on lithium and lithia appears analogous to its action on potassium and potassa, but the compounds have not been precisely examined.

SULPHATE OF LITHIA (*L+S'*) crystallizes in small rectangular prisms, perfectly white, and possessed of much lustre. Their taste is saline, and their solubility intermediate between that of sulphate of potassa and sulphate of soda. The crystals contain no water, and fuse at a heat below redness. Their solution occasions no change in solution of platinum, nor in tartaric acid. The anhydrous salt consists of

						C. Gmelin.	Hermann.			
Lithia	.	1	..	16	..	28.57	..	27.94	..	26
Sulphuric Acid	.	1	..	40	..	71.43	..	72.06	..	74
		<u>1</u>		<u>56</u>		<u>100.00</u>		<u>100.00</u>		<u>100.</u>

According to Gmelin, the crystals of sulphate of lithia contain 1 equivalent of water, or 14.4 *per cent*.

BISULPHATE OF LITHIA ( $L+2S'$ ) has been described as crystallizing in hexangular tables; but Berzelius denies that it is a distinct salt: he, however, admits that sulphate of lithia forms larger crystals when the solution contains excess of acid.

PHOSPHATE OF LITHIA has been examined by Dr. Gmelin: it may be obtained by adding phosphoric acid to sulphate of lithia; no precipitate is at first formed, but on adding excess of ammonia, an insoluble *phosphate of lithia* falls. This property enables us to separate lithia from potassa and soda. The phosphate of lithia may be decomposed by dissolving it in acetic acid, and adding acetate of lead: *acetate of lithia* remains in solution.

BIPHOSPHATE OF LITHIA is obtained in small crystals by dissolving the phosphate in phosphoric acid.

CARBONATE OF LITHIA. ( $L+car'$ .) When a strong solution of carbonate of ammonia is added to sulphate of lithia, a white precipitate of *carbonate of lithia* is formed. It requires about 100 parts of water at  $60^{\circ}$  for its solution. It is insoluble in alcohol. It is fusible, alkaline, effervesces with acids, and absorbs carbonic acid from the air. A solution of this carbonate, containing only 1-1000th of its weight, acts strongly upon vegetable colours. It is decomposed by lime and baryta. It consists of

					C. Gmelin.	Hermann.			
Lithia . . .	1	..	16	..	42.11	..	45.54	..	39
Carbonic Acid	1	..	22	..	57.89	..	54.46	..	61
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		38		100.00		100.00		100

BICARBONATE OF LITHIA. Carbonate of lithia is slightly soluble in water impregnated with carbonic acid. It is said to occur in this state in some mineral waters in Bohemia. By spontaneous evaporation, the carbonate separates in the form of a crystalline crust.

BORATE OF LITHIA much resembles borate of soda.

CHARACTERS OF THE SALTS OF LITHIA. It appears from the preceding statement, that lithia is distinguished from potassa and soda by its greater saturating power in respect to acids: that is, by its lower equivalent number; and by forming difficultly-soluble salts with phosphoric and carbonic acids. Chloride of lithium is highly deliquescent, and dissolves in strong alcohol, which enables us to separate it from the chlorides of potassium and of sodium. This solution burns with a purplish flame, and the same tint is communicated to the flame of the blowpipe when any salt of lithia is fused upon a thin slip of platinum-foil; they also corrode that metal, and leave a yellow spot at the point of action. Lithia is distinguished from the alkaline earths by forming soluble salts with sulphuric and oxalic acids, and by the alkaline re-action of its carbonate upon vegetable colours. Its salts are not precipitated by ferrocyanuret of potassium, nor by infusion of galls, nor by chloride of platinum, nor by caustic potassa: the precipitate, by carbonate of ammonia, re-dissolves when the liquid is diluted and boiled.

## § IV. CALCIUM.

THE existence of *calcium*, as the metallic base of lime, was first demonstrated by Davy in 1808; he found that when lime was rendered electro-negative in contact with mercury, an amalgam was formed, which, by distillation, afforded a white metal: when this metal was exposed to air, and gently heated, it burned, and produced the *oxide of calcium*, or *lime*. Our knowledge of calcium, is almost limited to this single experiment, and it has never been obtained in sufficient quantity to ascertain its general properties: its *equivalent* as determined by indirect but very satisfactory evidence, to which, we shall presently recur, may be considered as = 20. (20.5, Turner and Gmelin.)

CALCIUM AND OXYGEN; LIME; QUICK LIME; OXIDE OF CALCIUM. (*cal*+*o*) or C. Lime may be obtained in a state of considerable purity by exposing powdered white marble to a white-heat for an hour, in an open crucible, which expels the carbonic acid. To obtain absolutely pure lime, white marble may be dissolved in dilute muriatic acid, a little caustic ammonia added to the solution, and filtered: carbonate of ammonia is then added, and the precipitate dried, washed, and exposed for a sufficient time to a white-heat. This exposure to heat should take place in an open vessel, for in a close vessel, out of the contact of air, the decomposition of carbonate of lime is very imperfect: indeed, powdered marble may be kept for many hours at a red-heat, without losing any carbonic acid, provided air and moisture be carefully excluded. To obtain lime perfectly free from all traces of carbonic acid, the carbonate should first be heated in an open vessel, the lime thus obtained converted into a *hydrate*, and this again heated: all carbonic acid is thus effectually expelled. Pure lime is white, or of a very pale gray tint; it is acrid and caustic, and converts the vegetable blue tests to green; its specific gravity is 2.3; it is very difficult of fusion, but remarkably promotes the fusion of most other earthy bodies, and is therefore used in several metallurgic processes as a cheap and powerful flux. When quite pure it can only be fused in very minute particles by the oxygen blow-pipe, or by the Voltaic flame. When intensely heated, as for instance, by the oxyhydrogen blow-pipe, it is remarkable for its luminosity; and at this very high temperature a minute quantity is volatilized (see p. 206.) It is an essential ingredient in mortar and other cements used in building. Exposed to air it absorbs water and carbonic acid.

From the concurrent testimony of different analysts the number 28 is assumed, as the equivalent of lime; and as it is the *protoxide* of calcium, it consists of

					Berzelius.	Davy.				
Calcium	.	1	..	20	..	71.4	..	71.91	..	72.8
Oxygen	.	1	..	8	..	28.6	..	28.09	..	27.2
		<u>1</u>		<u>28</u>		<u>100.0</u>		<u>100.00</u>		<u>100.0</u>

HYDRATE OF LIME; SLAKED LIME. (C+*q*.) When a small quantity of water is poured upon lime there is a great rise of temperature resulting from the solidification of a portion of the water, and a bulky white-powder is obtained, which is a *hydrate*.

Hydrate of lime may be obtained in a crystalline form by placing lime-water under the receiver of an air-pump, containing another vessel of sulphuric acid. The water is thus slowly evaporated, and imperfect six-sided crystals are formed. (Gay Lussac, *Ann. de Chim. et Phys.*, i. 334.) In composition these crystals resemble the pulverulent hydrate. Exposed to the air, they gradually crumble down into carbonate of lime. Hydrate of lime is a compound of

				Dalton.	Gay Lussac. <i>Crystallized.</i>
Lime	.	1	.. 28	.. 75.6	.. 75
Water	.	1	.. 9	.. 24.4	.. 25
		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
		1	37	100.0	100
				<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
				100	100.00

**LIME-WATER.** At a temperature of  $60^{\circ}$ , 750 parts of water are required for the solution of one part of lime. Boiling water, however, as Mr. Dalton first observed (*New System of Chem. Phil.*) does not dissolve so large a quantity; one part of lime requires, according to Phillips, 1280 parts of water at  $212^{\circ}$  for its solution (*Ann. of Phil. N. S.*, i. 107;) and water at  $32^{\circ}$  has its solvent power much augmented, one part of lime being soluble in 656 of water at that temperature. When lime-water is boiled, a portion of the lime is therefore precipitated; or aggregated, according to Phillips, into small crystalline grains. The cause of this crystallization he refers "to the effect which heat sometimes produces, of increasing instead of diminishing the attraction of cohesion, where this attraction is associated with a tendency to crystallize. This crystalline attraction, increased by that of the lime for a definite portion of water, is then greater than the attraction of the hydrate of lime for the water of solution, and the consequence is that crystals are formed." Lime-water is limpid and colourless; its taste is nauseous, acrid, and powerfully alkaline, and it converts vegetable blues to green. It is usually prepared by pouring warm water upon powdered lime, and allowing the mixture to cool in a close vessel; the clear part is then decanted from the remaining undissolved portion of lime. When lime-water is exposed to the air, a pellicle of carbonate of lime forms upon its surface, which, if broken, is succeeded by others, until the whole of the lime is thus separated in the form of an insoluble carbonate. Lime-water is used in medicine as an antacid. What is termed *milk or cream of lime*, is merely hydrate of lime diffused through lime-water.

**PEROXIDE OF CALCIUM.** ( $C + 2O$ ) When oxygen is passed over heated lime, it is absorbed, and a portion of *peroxide of calcium* is formed. A hydrated peroxide of calcium is thrown down in the form of small brilliant scales, according to M. Thenard, when lime-water is dropped into oxygenated water. Peroxide of calcium consists of

				Thenard.
Calcium	.	.	1 .. 20	.. 55.5
Oxygen	.	.	2 .. 16	.. 44.5
		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
		1	36	100.0

**CHLORIDE OF CALCIUM.** ( $cal + c.$ ) This compound occurs in sea-water and in some mineral waters; it is produced artificially by heating lime in chlorine, in which case oxygen is evolved; or by evaporating *muriate of lime*, (obtained by dissolving carbonate of lime in

muriatic acid,) to dryness, and exposing the dry mass to a red heat in closed vessels. It has a strong attraction for water; it deliquesces when exposed to air, and becomes what used to be called *oil of lime*. Hence it is that fused chloride of calcium, broken into small pieces, is frequently employed to deprive gases of their aqueous vapour; but when thus used, its absorptive powers in regard to some gases must not be overlooked. Its taste is bitter and acrid; one part of water, at 60°, dissolves four parts of the chloride. Its solubility, however, is greatly influenced by temperature, for at 32° one part of water will not dissolve more than two of the salt, and at 212° it takes up nearly any quantity. It is copiously soluble in alcohol, and much heat is evolved during the solution. When fused it acquires a phosphorescent property, as was first observed by Homberg, and hence it was termed *Homberg's phosphorus*. It is abundantly produced in the manufacture of carbonate of ammonia, from the decomposition of muriate of ammonia by lime, and hence has sometimes been called *fixed sal ammoniac*. Chloride of calcium consists of

						Ure.
Calcium . . . . .	1	..	20	..	35.7	.. 36.7
Chlorine . . . . .	1	..	36	..	64.3	.. 63.3
	1		56		100.0	100.0

Pelletier has stated, that if carbonic acid be passed through a solution of muriate of lime, the whole becomes a hard solid mass. If sulphuric acid be poured into a strong solution of muriate of lime, the whole congeals into a solid mass of sulphate of lime.

HYDRATED CHLORIDE OF CALCIUM is obtained by evaporating the aqueous solution to the consistence of a thick syrup; on cooling it concretes into a crystalline mass, which may be reduced to powder: in this state it is used in frigorific mixtures, to mix with snow. (p.155.) By careful management, or by exposing the strong solution to a cold of 32°, it may be obtained in prismatic crystals, consisting of

Chloride of calcium . . . . .	1	..	56	..	50.9
Water . . . . .	6	..	54	..	49.1
	1		110		100.0

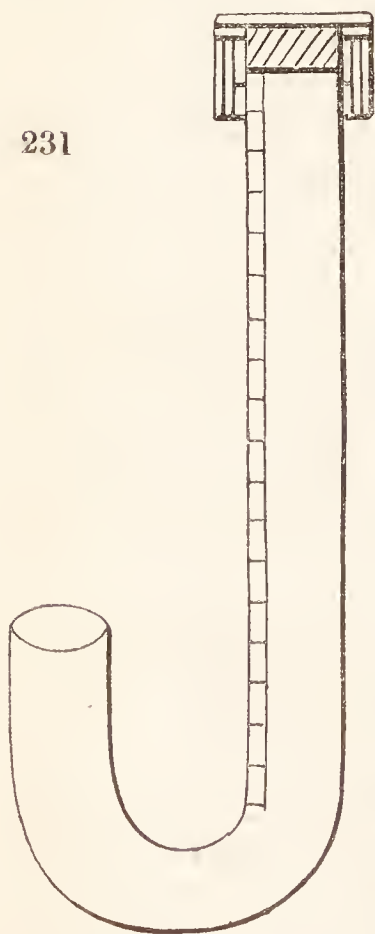
AMMONIA CHLORIDE OF CALCIUM. Faraday has shown (*Quart. Journal*, v. 74) that chloride of calcium absorbs large quantities of ammoniacal gas, during which it swells, cracks, splits in all directions, and at last crumbles down into a white powder. Exposed to the atmosphere it deliquesces less rapidly than the original chloride. Thrown into water it dissolves, forming a strong alkaline solution. Heated, it gives off ammonia, and the chloride remains unchanged. Immersed into chlorine, the ammonia burns off with a pale-yellow flame. Twenty grains of the compound furnished, when heated, about twenty cubic inches of ammonia. Mr. Faraday availed himself of this compound for the purpose of condensing ammonia into a liquid. It appears to consist of

Chloride of calcium . . . . .	1	..	56
Ammonia . . . . .	4	..	68
	1		124

CHLORIDE OF LIME; OXYMURIATE OF LIME. This compound is abundantly employed as a bleaching-material, and manufactured by passing chlorine into chambers containing hydrate of lime in fine powder, by which the gas is copiously absorbed with extrication of heat. It is a dry white powder, smelling feebly of chlorine, and having an acrid taste: it is partially soluble in water, and the solution, which is used under the name of *bleaching-liquor*, contains both chlorine and lime. Exposed to air it slowly evolves chlorine and absorbs carbonic acid; ultimately some chloride of calcium is formed, and it deliquesces. When heated, it gives off oxygen, and chloride of calcium results, an experiment which shows the superior attraction of calcium for chlorine as compared with oxygen, the latter being expelled from the lime.

Dr Ure has contrived an instrument for the speedy analysis of this salt for the purposes of the artist, by which the quantity of chlorine in any given sample may be determined. (*Quarterly Journal*, xiii. 21.)

“It consists of a glass tube, of about five cubic inches capacity, shaped as in the adjoining figure, and graduated into cubic inches and tenths. It is to be closed at top with a brass screw cap, and, at its



recurved end below, with a good cork. Pour mercury into the upper orifice, till the tube be nearly full, leaving merely space to insert ten grains of the bleaching-powder, made into a pellet-form with a drop of water. Screw in the cap-plug rendered air-tight by leather. Remove now the cork from the lower end, (also full of mercury,) and replace a little of the liquid metal by dilute muriatic acid (specific gravity 1.1). By dexterous inclination of the instrument, the acid is made to flow up through the mercury. Instantly on its coming into contact with the pellet, the chlorine is disengaged, the mercury flows out into a basin ready to receive it, while the resulting film of muriate of lime protects the surface of the metal almost completely from the gas. With an apparatus of this kind, which indeed is the same as that which I have long used for analysing limestones and marbles (see article *Carbonate* in my *Chemical Dictionary*), I get good accordances with the results derived from the loss of weight suffered

by a like quantity of the chloride, when it is dissolved in dilute muriatic acid. Since a cubic inch of chlorine may be estimated in round numbers at  $\frac{3}{4}$  of a grain, we may expect 10 grains of bleaching-powder to yield from 3 to 4 cubic inches of that gas, or by weight, from 20 to 30 per cent., a wide range of power, which it is well worth the bleacher's or paper-maker's while to ascertain. If carbonic acid be suspected, we need only agitate the mercury through the gas, adding some of the metal from time to time as the absorption proceeds. The carbonic acid will remain uncondensed at the top, and may be estimated in the usual way.”

Another mode of determining the commercial value of chloride of lime, consists in ascertaining its bleaching power by its effect upon a



solution of indigo; directions for this purpose have been drawn up by Gay Lussac. (*Ann. of Phil.*, xxiv., 218). Morin (*Ann. de Chim. et Phys.*, xxxvii., 142,) tests it by solution of protochloride of manganese, determining its proportion of chlorine by the quantity of peroxide of manganese which it throws down; but the free lime present seriously interferes with the practical application of this test.

The composition of bleaching-powder has been variously stated. Mr. Dalton (*Ann. of Phil.*, i. 15, and ii. 6) considers it as a *hydrated subchloride of lime*, containing two proportionals of lime and one of chlorine; and the same opinion is adopted by Thomson (*Ann. of Phil.* xv., 401), and by Welter (*Ann. de Chim. et Phys.*, vii., 383). Dr. Ure, however, shows, in the paper already quoted, that the quantity of chlorine absorbed is variable; he analyzed a specimen of good commercial bleaching-powder, and found it composed of 46 lime, 23 chlorine, and 31 water: a specimen prepared by himself with pure hydrate of lime contained 45.40 lime 40.32 chlorine, and 14.28 water, and he found the condensation of chlorine to vary with the pressure, the degree of exposure, and the quantity of water present. Upon the whole, it is not improbable that bleaching-powder consists of a chloride of lime, containing one proportional of chlorine and one of lime, mixed with a varying proportion of hydrate of lime; and that when water acts upon the compound the solution contains a chloride of lime. Berzelius regards bleaching-powder as a compound of chloride of calcium and *chlorite* of lime, and this opinion is said to be sanctioned by Balard's researches already quoted (p. 335), but if chlorite or hypochlorite of lime were formed by the action of chlorine upon pulverulent hydrate of lime, a large proportion of chloride of calcium must at the same time be produced, and we have no evidence of the existence of chloride of calcium in well-made bleaching-powder. A specimen of chloride of lime of the best quality usually sold in London, consisted of 1 equivalent of chlorine, 2 of lime, and 2 of water.

CHLORATE OF LIME is a very soluble deliquescent salt of a sharp bitterish taste. It is most easily produced by dissolving carbonate of lime in chloric acid. Exposed to heat, oxygen is evolved, and a chloride formed.

IODIDE OF CALCIUM (*cal + i*) is obtained by dissolving carbonate of lime in hydriodic acid, evaporating to dryness, and heating the residue in a close vessel till it fuses; it may also be obtained by digesting hydrate of lime with protiodide of iron: it is a deliquescent gray substance, which, heated in the air, absorbs oxygen and evolves iodine.

Dissolved in water and slowly evaporated, it furnishes deliquescent crystals, usually called *hydriodate of lime*; they are composed of the iodide and water. The iodide consists of

Calcium . . .	1	. . .	20	. . .	13.8
Iodine . . .	1	. . .	125	. . .	86.2
	<hr/>		<hr/>		<hr/>
	1		145		100.0

IODATE OF LIME. (*C + i'*.) This salt is formed by dissolving carbonate of lime in iodic acid; it also gradually crystallizes out of a mixed solution of iodate of potassa and chloride of calcium: it forms small

prismatic crystals soluble in 5 of cold and 1 of boiling water, and containing 3 *per cent.* of water. (Gay Lussac *Ann. de Chimie*, vol. xci., p. 84.)

BROMIDE OF CALCIUM (*cal* + *b*) was obtained by M. Henry by digesting hydrate of lime in a solution of protobromide of iron; it forms deliquescent acicules soluble in alcohol and water; it fuses and is partially decomposed when heated in open vessels.

BROMATE OF LIME (*C* + *b'*) has not been examined.

FLUORIDE OF CALCIUM; FLUOR SPAR. (*cal* + *f*.) This compound may be produced artificially by saturating dilute hydrofluoric acid with newly-precipitated and moist carbonate of lime, and may thus easily be collected, and dried in the form of white powder. If obtained by precipitating a neutral salt of lime with a soluble fluoride, it forms a gelatinous mass, the precipitation of which is accelerated by the addition of caustic ammonia. *Native fluoride of calcium*, or *fluor-spar*, is a mineral found in many parts of the world, but in great beauty and abundance in England, and especially in Derbyshire. Here it is commonly called *Derbyshire spar*, or by the miners of that county *blue John*. It is usually found in cubic crystals, which may easily be cleaved into octoëdra, sometimes considered as its primitive form. Its colours are extremely various. Its specific gravity = 3. It phosphoresces when exposed to a heat a little below redness (p. 199), and at a red-heat it fuses: it is sometimes used as a flux for promoting the fusion of other minerals, hence its German name *Flusspath*, and the English *Fluor*. It generally occurs in veins; in the Odin mine at Castleton, in Derbyshire, it is found in detached masses, from an inch to more than a foot in thickness; their structure is divergent, and the colours, which are various, disposed in concentric bands. It is the only variety which admits of being turned in the lathe into vases and other ornamental articles. *Compact fluor* is a scarce variety: the finest specimens come from the Hartz. A third variety is *chlorophane*, so called from the beautiful pale-green light which it exhibits when heated. The nature of the colouring-matter of blue and green fluor spar is not exactly understood. It is liable to fade, and the blue varieties become red and brown by heat.

Fluoride of calcium exists, according to Berzelius, in bones, urine, and the enamel of the teeth, in the human subject; he also found it in minute quantities in some of the Carlsbad waters.

Pure fluoride of calcium is not decomposed by cold sulphuric acid, but forms with it a transparent viscid mixture. At a temperature of about 100° its decomposition begins, sulphate of lime forms, hydrofluoric acid is evolved, and the mixture grows opaque. If the fluor-spar contain silica, then sulphuric acid immediately acts upon it, evolving silico-fluoric acid. Concentrated muriatic and nitric acids dissolve fluoride of calcium without decomposition, and become milky when diluted; but it is doubtful whether such solutions are formed when the fluoride is perfectly pure. It is scarcely soluble in hydrofluoric acid. Fused with carbonate of potassa, carbonate of lime and fluoride of potassium are produced. It is now generally admitted to be a binary compound of calcium and fluorine, consisting of

						Davy.
Calcium . . .	1	..	20	..	52.6	53.313
Fluorine . . .	1	..	18	..	47.4	46.687
	<hr/>		<hr/>		<hr/>	<hr/>
	1		38		100.0	100.000

NITRATE OF LIME. ( $C + n'$ .) This is a deliquescent salt, soluble in one-fourth its weight of water at 60°. It is found in old plaster and mortar, from the washing of which, nitre is procured by the addition of carbonate of potassa.

The production of this salt in artificial nitre-beds has already been adverted to (p. 548). It may be crystallized, by very slow evaporation, in six-sided prisms, containing according to Bergman about 25 per cent. of water, but when obtained from a solution evaporated very low, and set aside in the cold, it appears in the form of groups of acicular crystals. It is soluble in alcohol. When exposed to a moderate heat, it undergoes watery fusion; the water then evaporates and the salt fuses; on cooling it concretes into a semi-transparent phosphorescent substance, called from the discoverer of this property *Balduin's phosphorus*. (Birch's *History of the R. S.*, iii., 328.) At a red heat it is decomposed; its acid is dissipated, and pure lime remains. It has been found in some mineral waters. Anhydrous nitrate of lime consists of

						Wenzel.
Lime . . . . .	1	..	28	..	34.1	33.8
Nitric acid ..	1	..	54	..	65.9	66.2
	<hr/>		<hr/>		<hr/>	<hr/>
	1		82		100.0	100.0

SULPHURET OF CALCIUM ( $cal + s$ ) is formed by passing sulphuretted hydrogen, or the vapour of sulphuret of carbon, over red-hot lime. It is also formed by the action of charcoal or of hydrogen upon *sulphate of lime* at a red-heat. It is of a yellow or orange tint, slowly acted upon by water, and of an hepatic and alkaline taste. When its solution is carefully evaporated in vacuo, small cubic crystals of hydrosulphuret of lime are obtained.

HYDROSULPHURET OF LIME ( $\overline{cal + o} + \overline{s + h}$ ) is also obtained by passing sulphuretted hydrogen through a mixture of quicklime and water. The solution has an hepatic, acrid, and bitter taste.

When three parts of slaked lime and one of sulphur are boiled in twenty parts of water, and the solution allowed to cool upon the sediment, crystals are formed, which may be dried by exposure to the absorbent power of a large surface of sulphuric acid, placed under an exhausted receiver. Their form is that of quadrilateral prisms, with dièdral summits. They are sparingly soluble in cold water, the solution having a yellow colour, and an acrid, bitter, and sulphurous taste. They consist, according to Herschel (*Edin. Phil. Journ.*, i., 11), of

						Herschel.
Lime . . .	2	..	56	..	44.80	42.9
Sulphur . .	2	..	32	..	25.60	26.0
Hydrogen . .	1	..	1	..	0.75	0.6
Water . . .	4	..	36	..	28.85	30.5
	<hr/>		<hr/>		<hr/>	<hr/>
	1		125		100.00	100.0

So that, excluding water, these crystals contain 2 atoms of lime and 1 atom of bisulphuret of hydrogen.

**HYPOSULPHITE OF LIME.** ( $C + \underline{S}$ .) When sulphurous acid is ground in a mortar with the above crystals its smell disappears, and when filtered it is found to be a solution of *hyposulphite of lime*. By passing sulphurous acid through an aqueous solution of sulphuret of lime, the same product is obtained; and if the solution be filtered and evaporated, at a temperature not exceeding  $140^{\circ}$ , it furnishes crystals: the temperature of ebullition decomposes it. The crystals are little altered by air, very soluble in water, and insoluble in alcohol. They consist of

			Herschel.
Lime . . . . .	1	..	21.8
Hyposulphurous acid . . . . .	1	..	36.8
Water . . . . .	6	..	41.4
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		100.0

**SULPHITE OF LIME** ( $C + \underline{S}$ ) is formed by passing sulphurous acid into a mixture of lime and warm water, or by mixing the solutions of chloride of calcium and sulphite of potassa. It is a white powder, soluble by excess of sulphurous acid, and then separating in prismatic crystals, of difficult solubility, efflorescent, and passing into sulphate of lime by exposure to air.

**HYPOSULPHATE OF LIME.** ( $C + \underline{S}'$ .) This salt is formed by decomposing hyposulphate of manganese by lime, filtering, and evaporating the solution: it forms transparent dodecaëdral crystals, permanent in the air, soluble in 2.46 of water at  $60^{\circ}$ , and insoluble in alcohol. (Heeren, *Poggend.*, vii., 178.) The crystals consist of

Lime . . . . .	1	..	20.5
Hyposulphuric acid . . . . .	1	..	53.0
Water . . . . .	4	..	26.5
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		100.0

**SULPHATE OF LIME** ( $C + \underline{S}'$ ) occurs native in *selenite*, *gypsum*, *plaster-stone*, &c. It is easily formed artificially, by dropping sulphuric acid upon lime, in which case there is great evolution of heat; or by decomposing a solution of chloride of calcium, or any of the soluble salts of lime, by sulphuric acid or by a soluble sulphate. When thrown down from its solutions, or in any way slowly deposited, it generally forms minute silky crystals soluble in 350 parts of water. When these, or the *native crystallized sulphate* are exposed to a dull-red heat, they lose water, and fall into a white powder (*plaster of Paris*), which, made into a paste with water, soon solidifies; and when in large quantity, with very sensible increase of temperature. Hence its use in taking casts for busts, figures, and ornaments. Exposed to a very high temperature, short of its fusing-point, it loses this property of recombining with water. Anhydrous sulphate of lime requires about 500 parts of water at  $60^{\circ}$ , and 450 parts at  $212^{\circ}$ , for its solution: and, according to Mr. Paul, (*Phil. Mag.*, xv., 63,) if this solution be saturated by pressure with hydrogen, the sulphate in about six months is converted into a sulphuret. As sulphate of lime is more soluble in water than pure lime, sulphuric acid affords no precipitate when added to *lime-water*. Nearly all spring and river water contains this salt, and in those waters which are called *hard* it is abundant. It gives to them a slightly nauseous taste. At a very high temperature sulphate of

lime is fusible, but it suffers no decomposition; heated with charcoal it is converted into a sulphuret of calcium. It dissolves without decomposition in dilute nitric and muriatic acids, and separates from these solutions when concentrated, in long silky or transparent crystals. It is decomposed by the alkaline carbonates. Anhydrous sulphate of lime consists of

						Wenzel.	Bergman.	
Lime	.	1	..	28	..	41.1	..	41
Sulphuric acid	.	1	..	40	..	58.9	..	59
		<u>1</u>		<u>68</u>		<u>100.0</u>		<u>100.</u>

And the crystallized sulphate of lime consists of

						Klaproth.	Bergman.	
Anhydrous sulphate of lime	.	1	..	68	..	79	..	78
Water	.	2	..	18	..	21	..	22
		<u>1</u>		<u>86</u>		<u>100</u>		<u>100.</u>

NATIVE SULPHATE OF LIME occurs in various forms. The *crystallized* or *hydrone* variety ( $C + S' + 2Q$ ) is usually called *selenite*\*; the fibrous and earthy, *gypsum*†; and the granular or massive, *alabaster*‡. The primitive form of selenite is a rhomboidal prism of  $113^{\circ} 8'$  and  $66^{\circ} 52'$ . The crystals are commonly transparent, and of various colours; it is softer than native carbonate of lime, and yields very easily to the nail. It is seldom found in veins, but generally disseminated in argillaceous strata. It occurs in Cumberland at Alston, and in Oxfordshire at Shotover Hill, where it is often accompanied by shells and pyrites, and appears to have resulted from their mutual decomposition. A beautiful fibrous variety, called *satin-gypsum*, is found in Derbyshire, applicable to ornamental purposes, such as beads, broaches, &c. *Massive and granular gypsum* is found in this country accompanying the salt-deposits in Cheshire. It abounds at Montmartre, near Paris, and contains organic remains; sometimes it forms entire hills. In the Tyrolese, Swiss, and Italian Alps, it is found upon the primitive rocks, often of the purest white, especially at Montier, near Mont Blanc, and near the summit of Mont Cenis. It is turned by the lathe, and sculptured into a variety of beautiful forms, more especially by the Florentine artists. Columns for interior architecture are sometimes formed of it, as may be seen in the hall of Kedleston-house in Derbyshire.

There is a variety of sulphate of lime, which has been called *anhydrous gypsum*, or *anhydrite*, in reference to its containing no water. It is harder than selenite, and sometimes contains common salt, and is then called *muriacite*. It is rarely crystallized, generally massive and lamellar, and susceptible of division into rectangular prisms. It has been found in Derbyshire and Nottinghamshire of a pale-blue tint; sometimes it is pink or reddish, and often white. It has been found at Vulpino in Italy, and hence called *Vulpinite*. The statuarics of Bergamo and Milan employ it, and artists know it by the name of *Marbre di Bergamo*. A compound of sulphate of lime and sulphate of soda is found in the salt-mines of

\* From  $\sigma\epsilon\lambda\eta\nu\eta$ , *the moon*, in reference to its soft lustre.

† From  $\gamma\eta$ , *earth*, and  $\epsilon\psi\epsilon\iota\nu$ , *to concoct*: formed, or concocted in the earth.

‡ An ancient term applied to vases or boxes, for containing perfumes: perhaps from *a*, *privative*, and  $\lambda\alpha\beta\omicron\nu$ , *a handle*: as opposed to vessels *with handles*.

New Castile, which mineralogists have described under the name of *Glauberite*.

PHOSPHURET OF CALCIUM. (*cal + p.*) By passing phosphorus over red-hot lime, a brown compound is produced, which rapidly decomposes water with the evolution of phosphuretted hydrogen gas, and which consists of phosphuret of calcium and phosphate of lime; the oxygen of the lime at this high temperature converts a portion of the phosphorus into phosphoric acid, and the evolved calcium combines with another portion of phosphorus to form phosphuret of calcium. *Hydrophosphuret* and *hypophosphite of lime* are formed by its action upon water, and a phosphate of lime precipitates. When dilute muriatic acid is poured upon this phosphuret, abundance of *phosphuretted hydrogen* is also liberated (p. 450).

The best process for obtaining phosphuret of calcium is the following: select a green-glass, or porcelain tube, closed at one end, and about eighteen inches long, and one inch diameter, and carefully cover it with a clay lute containing a very little borax. Put an ounce of phosphorus broken into small pieces into the lower end, and fill it up with pieces of clean quick-lime, about the size of large peas: place it in an inclined position in a furnace, so that the end containing the phosphorus may protrude, while the upper part of the tube is heating to redness; then slowly draw the cool part into the fire, by which the phosphorus will be volatilized, and passing into the red-hot lime, convert a portion of it into phosphuret. Care should be taken that no considerable portion of phosphorus escapes and burns away at the open end of the tube, which, after the process, should be corked and suffered to cool. Its contents may then be shaken upon a sheet of paper, and the brown pieces picked out, and carefully preserved in a well-stopped phial; the white pieces, or those which are only pale-brown, must be rejected. The composition of phosphuret of calcium has not yet been experimentally determined.

HYPHOPHOSPHITE OF LIME may be obtained by boiling phosphorus in thin cream of lime, filtering off the solution, and passing carbonic acid through it, to separate excess of lime. The clear solution evaporated in vacuo furnishes crystals of the hypophosphite. This salt is useful for the preparation of other hypophosphites. It is insoluble in alcohol.

PHOSPHITE OF LIME is a difficultly-soluble salt, crystallizable by spontaneous evaporation. When its solution is heated, nacreous crystals of a *subphosphite* are deposited, and a very soluble and difficultly-crystallizable *biphosphite* remains dissolved.

PHOSPHATE OF LIME. There appear to be several definite combinations of lime with phosphoric acid, among which the following have been particularly examined.

1. NEUTRAL PHOSPHATE OF LIME. (*C + p'*.) When a solution of rhombic phosphate of soda is dropped into a solution of chloride of calcium, the latter being left in excess, a crystalline precipitate falls, which at a red-heat loses water: it is white, tasteless, and consists of

	Berzelius.				Berzelius.				
Lime . . . . .	1	28	43.7	45.81	. . . . .	1	28	34.2	35.42
Phosphoric acid	1	36	56.3	54.19	. . . . .	1	36	43.9	41.90
Water . . . . .	0	0	0.0	0.0	. . . . .	2	18	21.9	22.68
	<hr/>					<hr/>			
Anhydrous	1	64	100.0	100.00	Crystallized	1	82	100.0	100.00

2. SUBPHOSPHATE OF LIME;  $\frac{2}{3}$  PHOSPHATE OF LIME; BONE PHOSPHATE. ( $1\frac{1}{2}C + p'$ .) This phosphate exists in bones and other parts of animals: it is formed when a solution of chloride of calcium is gradually dropped into the solution of rhombic phosphate of soda, the latter being left in excess; or whenever ammonia is added to any acid solution of phosphate of lime; or by adding neutral phosphate of ammonia to solution of chloride of calcium, in which case the fluid becomes acid. The tendency of phosphoric acid to form a basic or subsalt with lime is such, that if moist neutral phosphate of lime be mixed with a strong solution of chloride of calcium, muriatic acid is evolved on heating the mixture. This salt is white and insipid, and when recently precipitated, and boiled in water, a trace of it remains in solution, and if gelatine or starch be present a very sensible portion is taken up. Water, containing common salt or muriate of ammonia, also sparingly dissolves it. Dilute nitric muriatic and acetic acids dissolve it without decomposition, and ammonia throws it down unaltered. It is decomposed when digested in solution of sulphate of ammonia. Sulphuric acid converts it into sulphate and superphosphate of lime. At a very high temperature it fuses into a white opaque enamel. It is composed of

						Berzelius <i>Artificial.</i>		Fuchs. <i>Artificial.</i>		Klaproth. <i>Apatite.</i>	
Lime . . . . .	$1\frac{1}{2}$	..	42	..	53.8	..	51.68	..	54.74	..	53.75
Phosphoric acid	1	..	36	..	46.2	..	48.32	..	45.26	..	46.25
	1		78		100.0		100.00		100.00		100.00

*Native Phosphate of Lime*, identical in composition with the preceding, occurs crystallized and massive, and is known under the names of *apatite*, *asparagus-stone*, *moroxite*, and *phosphorite*. The crystallized variety is found in Cornwall and Devonshire, of singular beauty. Its primitive form is a six-sided prism: it also occurs in volcanic products; and, what is curious, the former is phosphorescent, and the latter not. The massive variety is found in Bohemia and in Spain.

3. SESQUIPHOSPHATE OF LIME, ( $C + 1\frac{1}{2}p'$ .) is obtained by adding alcohol to a saturated solution of the *neutral* phosphate in phosphoric acid; the precipitate, when washed with alcohol, consists of 1 proportional of lime +  $1\frac{1}{2}$  phosphoric acid. Water throws down from it a more neutral salt. (Berzelius, *Ann. de Chim. et Phys.*, ii. 167.)

4. BIPHOSPHATE OF LIME, ( $C + 2p'$ .) is formed, according to Berzelius, by digesting the *neutral* phosphate in phosphoric acid. On evaporation, crystalline scales are deposited, composed of 1 proportional of lime + 2 of phosphoric acid. The same salt is said to be obtained by digesting the neutral phosphate in muriatic or nitric acids, and evaporating the solution till it furnishes crystals. Distilled with charcoal, its excess of acid is decomposed and yields phosphorus, and a neutral phosphate remains.

5. SUPERPHOSPHATE OF LIME. The phosphoric glass described under the head *Phosphorus* (p. 438), is considered by Dr. Thomson as a definite compound, which he has termed *quadriphosphate of lime*. (*System*, ii., 460.) If 100 parts of phosphate of lime be digested for twenty-four hours with 87 parts of sulphuric acid diluted with a

sufficient quantity of water, and be then filtered, the liquor which passes through contains the whole of the phosphoric acid, with only one-fourth of the lime which existed in the original salt; the remaining three-fourths having formed an insoluble compound with the sulphuric acid. The dissolved salt, therefore, is a compound of 1 atom of lime = 28 + 4 atoms of acid = 112. When evaporated, it forms, on cooling, pearly scales, which have an acid taste, and dissolve readily in water, giving an acid solution of the specific gravity 1.44. When dried and fused in a crucible, a transparent glass is obtained, commonly called *glacial phosphoric acid*, and employed chiefly in the production of phosphorus. (Henry, i., 567.) According to Berzelius, the decomposition of bone-earth by sulphuric acid, is not attended by any definite result, but varies with the concentration and quantity of the acid, and is nearly complete when concentrated acid is added to a saturated solution of the superphosphate. Phosphate of lime is entirely decomposed when digested in a mixture of sulphuric acid and alcohol; sulphate of lime is precipitated, and an alcoholic solution of phosphoric acid, free from lime, is obtained. The solution of phosphate of lime in nitric acid, is decomposed by carbonate or acetate of lead; the lime remains in solution with the nitric acid, and the phosphoric acid is precipitated in combination with the oxide of lead.

**SELENITE OF LIME.** Berzelius has described a *neutral selenite* and a *biselenite of lime*. The former gradually falls in a pulverulent form, from a solution obtained by the action of selenious acid on carbonate of lime. If fused at a red-heat in a glass vessel, it corrodes and passes through it. When dissolved in selenious acid small prismatic crystals of *biselenite of lime* are obtained, which are permanent in the air; when heated, or digested in ammonia, they lose acid, and become neutral. (*Ann. de Chim. et Phys.*, ix., 263.) The *seleniates* of lime have not been examined, nor has the action of selenium upon calcium or lime.

**CARBONATE OF LIME, (C + car'),** is the most abundant compound of this earth; it is artificially formed, when lime-water is exposed to air; it becomes gradually covered with an insoluble film of carbonate of lime; hence its use as a test of the presence of carbonic acid. Excess of carbonic acid re-dissolves the precipitate, producing a supercarbonate. Carbonate of lime is also precipitated by the carbonated alkalis from solutions of muriate, nitrate, and sulphate of lime. It is a tasteless white powder, insoluble in water, and having no alkaline reaction. Exposed for a sufficient time to the joint action of a red-heat and a current of air, the whole of the carbonic acid escapes, to the amount of 44 per cent., and quicklime is obtained. Hence carbonate of lime consists of

					Kirwan.	Marcet.	Stromeyer.	Berzelius.					
Lime . . .	1	..	28	..	56	..	55	..	56.1	..	56.35	..	56.4
Carbonic acid	1	..	22	..	44	..	45	..	43.9	..	43.65	..	43.6
	<u>1</u>		<u>50</u>		<u>100.</u>		<u>100</u>		<u>100.0</u>		<u>100.00</u>		<u>100.0</u>

Mr. Daniell obtained artificial crystals of carbonate of lime, from a solution of lime in syrup: by exposing this solution to the air, Gay Lussac found the whole of the lime deposited in acute rhombic crystals, consisting of 1 atom of carbonate of lime and 5 of water (or 50 + 45.)



These crystals are not changed by cold water, but in hot water, or exposed to air, they gradually fall to powder. Boiled in alcohol they retain their form but lose 2 atoms of water, becoming  $(C + \text{car} + 3q.)$  (*Ann. de Chim. et Phys.*, xlvi., 301.)

*Native Carbonate of Lime* occurs in great abundance and in various forms. The primitive form of crystallized carbonate of lime, or *calcareous spar*, is an obtuse rhomboid of  $105^{\circ} 5'$  and  $74^{\circ} 55'$ . Its specific gravity is 2.72. It occurs in every kind of rock, and its secondary forms are more numerous than those of any other substance. Count Bournon, in his *Traité de Minéralogie*, has described and figured six hundred and eighty modifications. What is termed *Iceland spar* is this substance, in its primitive form, and of extreme purity: it is highly doubly refractive (p. 178) and transparent; some of the varieties are opaque or translucent, snow-white, or tinged of different hues. The mineral is recognised by its foliated fracture, and its moderate hardness: before the blowpipe it loses carbonic acid and becoming *lime*, is intensely luminous: it dissolves with effervescence in muriatic acid, and the solution, when much diluted, affords a white precipitate with oxalate of ammonia. Carbonate of lime sometimes forms *stalactites* and *stalagmites* (from *σταλαζω*, I drop, and *σταλαγμα*, a drop,) of which some of the caverns of Derbyshire furnish magnificent specimens; it is there deposited from its solution in water acidulated by the carbonic acid, and substances immersed in this water become incrustated by carbonate of lime, when the excess of acid flies off, as seen in the *petrifying well* at Matlock. A fibrous variety of carbonate of lime, called *satin-spar*, is found in Cumberland.

Another variety, originally found in Arragon in Spain, has been termed *Arragonite*; it often occurs in six-sided crystals, of a reddish colour, and harder than the common carbonate. There is an acicular or fibrous variety, found in France and Germany; and the white radiated substance, improperly called *flos ferri*, is also regarded as of the same species. Some varieties contain about 3 per cent. of strontia. The crystalline forms of Arragonite have been described in detail by Bournon, (*Traité de Minéralogie*.) They contain a little water, which they lose when heated, and fall to powder. This distinguishes Arragonite from calcareous spar. It is also a little heavier, its specific gravity being from 2.8 to 2.9.

All the varieties of *marble* and *limestone* consist essentially of carbonate of lime; of these, *white granular limestone*, or *primitive marble*, is most esteemed; there are, also, many coloured varieties of extreme beauty. It is distinguished from *secondary limestone* by the absence of all organic remains, by its granularly foliated structure, and by its association with other primitive substances. The most celebrated statuary marble is that of Paros and of Mons Pentelicus, near Athens; of these, some of the finest specimens of ancient sculpture are composed. The marble of Carrara, or Luni, on the eastern coast of the Gulf of Genoa, is also much esteemed; it is milk-white and less crystalline than the Parian.

Many beautiful secondary marbles for ornamental purposes are quarried in Derbyshire, and especially the *black marble*, called also

*Lucullite*, from the admiration bestowed on it by Lucius Lucullus. (Pliny, *Hist. Nat.*, 36, 8.) Its colour appears to depend upon a small quantity of carbonaceous matter. Westmoreland and Devonshire also afford beautiful varieties of ornamental marble; and in Anglesea, a marble intermixed with green serpentine is found, little inferior in beauty to the *verd antique*.

Among the inferior limestones, we enumerate many varieties, such as *common marble*; *bituminous limestone*, abundant upon the Avon, near Bristol, and known under the name of *swine-stone* or *stink-stone*, from the peculiar smell which it affords when rubbed; *Oolite* or *Roestone*, of which the houses of Bath are built; and its variety, called *Portland-stone*. *Pisolite* consists of small rounded masses, composed of concentric layers, with a grain of sand always in the centre; and lastly, *chalk* and *marl*.

All these substances are more or less useful for ornamental purposes, or for building; they afford *quicklime* when burned, and in that state are of great importance as *manures*, and as ingredients in the cements or *mortars* used for building. There is a great variety of limestones used for burning into quicklime, and, generally speaking, any of the varieties may be employed which neither fuse nor crumble into powder at the temperature required to expel the carbonic acid, which is a full red-heat.

*Lime-burning.* Although all the species of limestone may, by burning, be brought to the state of quicklime, the substances belonging to the family of *compact limestone* are the only ones that are employed for this purpose in the large way. Sometimes calcareous spar, and statuary marble, are used in the laboratory for the purpose of procuring a lime purer than ordinary. But, owing to the crystalline texture of these substances, the laminæ of which they are composed part from each other during the volatilization of the carbonic acid, so that by the time they are rendered caustic, their cohesion is destroyed, and they are reduced to the state of sand, a circumstance which must always prevent them from being used in kilns of the common construction. The lime-kiln at present almost universally employed in this country, is a cup-shaped concavity, in a solid mass of masonry, open at top, and terminated at bottom by a grate, immediately above which is an iron door. This simple furnace is first charged with fuel, (either wood, or coal and cinders, but more commonly the latter,) upon which is afterwards laid a stratum about a foot thick of limestone, broken into pieces not larger than the fist; to this succeeds a charge of fuel; and so on alternately, keeping the kiln always full. The pieces of limestone descend towards the bottom of the kiln in proportion as the fuel is consumed, being in the mean time kept at a pretty full red-heat. At this temperature, the water and carbonic acid are driven off; and by the time the limestone arrives at the bottom of the kiln, which happens in about forty-eight hours, it is rendered perfectly caustic. The door above the grate is then opened, and the lime below the next descending stratum of fuel is raked out; the remaining contents of the furnace sink down, and a fresh charge is laid on the top. The compact limestone, after having undergone this process, though much lighter and more porous than before, still retains its figure unaltered: hence it is readily separable from the ashes of the fuel,

and is sufficiently hard to be carried from place to place without falling to pieces. (See Aikin's *Dictionary*, Art. LIME.)

Attempts have been made to burn lime, or, in other words, to expel the carbonic acid from limestone, in close vessels, but it is invariably found that the carbonic acid cannot, under such circumstances, be driven off; and, indeed, Bucholz found, that upon strongly heating five or six pounds of pure chalk, closely pressed into a crucible, and out of the access of air and its watery vapour, scarcely any carbonic acid was driven off; but, with the exception of a small portion upon the surface the contents of the crucible were converted into a hard, foliated, yellowish mass, retaining nearly the whole of the carbonic acid, semi-transparent, and evidently having undergone incipient fusion. (Gehlen's *Jour.*, Second Series, i., 271.) This agrees with Sir James Hall's experiments, who, by exposing powdered chalk to great heat and pressure, succeeded in fusing it (without escape of carbonic acid), and thus imitating the process of nature, by which he supposed *marble* to have been formed.

CYANURET OF CALCIUM has not been obtained. When hydrate of lime is digested in hydrocyanic acid, a solution of hydrocyanate of lime is formed, which upon evaporation is resolved into ammonia and carbonate of lime.

SULPHOCYANATE OF LIME forms deliquescent acicular crystals, soluble in water and in alcohol. (*Sulphocyanuret of Calcium?*)

BORATE OF LIME is a white tasteless powder of very difficult solubility in water. At a red-heat it forms a vitreous mass.

FLUOBORATE OF LIME forms a gelatinous mass, which has an acid taste and reddens litmus. (Berzelius.)

CHARACTERS OF THE SALTS OF LIME. These salts have the following properties: those which are *soluble* are not altered by pure ammonia, but they are decomposed by potassa and soda. They are also decomposed by the carbonates of potassa, soda, and ammonia, which produce precipitates of *carbonate of lime*. Oxalate of ammonia produces in their solutions a white insoluble precipitate of *oxalate of lime*, which, exposed to a red heat, affords carbonate of lime or pure lime. Such of the salts as are soluble in alcohol, tinge the edge of its flame of a reddish colour. The *insoluble* salts of lime are decomposed by being boiled with carbonate of potassa, and afford *carbonate of lime*.

## § V. BARIUM.

THIS metal was discovered by Davy, in 1803; he obtained it by placing a globule of mercury upon moistened *baryta*, lying upon a plate of platinum, in connexion with the positive pole of a powerful Voltaic battery: the negative wire was then brought into contact with the mercury, which, combining with the evolved barium, gradually became an *amalgam*; this was heated out of the contact of air so as to distil off the mercury, and the barium remained.

Barium has a specific gravity above 2. It is of a gray colour, and rapidly absorbs oxygen; when gently heated it burns with a red light; it decomposes water, evolving hydrogen, and forming a solution of *baryta*:

its properties, however, have hitherto scarcely been ascertained. Its equivalent, deduced indirectly from its saturating power and from the action of chlorine on baryta, is 69. (68.6 Gmelin: 68.7 Turner.)

OXIDE OF BARIUM, BARYTA, or BARYA ( $ba + o$ ) or B, is obtained by exposing the crystals of pure *nitrate of baryta* for some time to a bright red-heat, or by subjecting artificial *carbonate of baryta* to an intense heat thoroughly mixed with about 10 per cent. of finely-powdered charcoal. It is of a gray colour, and, when pure, very difficult of fusion. Its specific gravity is about 4, hence the name *Baryta*, as being the *heaviest* of the substances usually called *earths* (from βαρυς, *heavy*). It has a strong alkaline taste, and reaction on vegetable colours. It is insoluble in alcohol. It eagerly absorbs water, heat is evolved, and a white hydrate is formed. Baryta, considered as a *protoxide of barium*, consists of

						Davy.	Berzelius.		
Barium . . .	1	..	69	..	89.6	..	89.7	..	89.55
Oxygen . . .	1	..	8	..	10.4	..	10.3	..	10.45
	1		77		100.0		100.0		100.00

HYDRATE OF BARYTA. When pure baryta is sprinkled with water it absorbs it, becomes intensely hot, and crumbles down into a bulky white powder, which fuses, but does not give out water at a red-heat. It is composed of

Baryta . . .	1	..	77	..	89.5
Water . . .	1	..	9	..	10.5
	1		86		100.0

Hydrate of baryta dissolves in 20 parts of cold, and in 3 of boiling, water, forming a solution which is a very delicate test of the presence of carbonic acid, and which speedily becomes covered with a film of carbonate of baryta when exposed to air. A saturated solution of baryta, in hot water, deposits flattened hexagonal prisms as it cools, containing, according to Dalton, 20, but according to Phillips, 10, equivalents of water. (*Phil. Mag.*, vi., 52, 3rd series.) *Baryta-water* is powerfully alkaline and poisonous.

PEROXIDE OF BARIUM. ( $ba + 2o$ .) This compound is obtained when baryta is heated in oxygen, or when dry oxygen gas is passed over fragments of baryta, heated to dull-redness in a glass or porcelain tube: it may also be formed by adding one part of chlorate of potassa to four of baryta, previously heated to redness in a platinum crucible; the oxygen of the chlorate combines with the baryta, and, by the action of water, the remaining chloride of potassium may be washed out, and a *hydrated peroxide of barium* remains, composed of 1 equivalent of baryta, 2 of oxygen, and 6 of water. (Wöhler and Liebig.) The application of this compound to the production of the *peroxide of hydrogen*, or *oxygenated water*, has already been pointed out. (p. 358.)

CHLORIDE OF BARIUM. ( $ba + c$ .) This compound may be obtained by heating baryta in chlorine, in which case oxygen is evolved; or in muriatic acid gas, when it becomes red-hot, and chloride of barium and water are the results. It is generally formed by dissolving carbonate of baryta in diluted muriatic acid, evaporating to dryness, and fusing the residue in a covered platinum crucible. It is a grayish-white substance,

of an acrid taste, not deliquescent by exposure to air; soluble without decomposition in water, and insoluble in alcohol. It is generally kept in aqueous solution which is in constant use in the laboratory as a test and precipitant for sulphuric acid: this, by evaporation, yields flat four-sided crystals, bevelled at their edges, and permanent in ordinary states of the atmosphere, but efflorescent, from the loss of water of crystallization, in a very dry air at 60°. At 212° the water is soon expelled. 100 parts of water at 60 dissolve about 40 parts of those crystals, and at 222°, which is the boiling-point of the saturated solution, 100 of water dissolve 78. The anhydrous chloride of barium consists of

Barium	.	.	1	..	69	..	65.8
Chlorine	.	.	1	..	36	..	34.2
			1		105		100.0

The crystals contain, according to Phillips, 14.5 per cent. of water (*Ann. of Phil., N. S., vi., 342*), and are, therefore, composed of

Chloride of Barium	.	.	1	..	105	..	85.4
Water	.	.	2	..	18	..	14.6
			1		123		100.0

CHLORATE OF BARYTA (B+C') was formed by Chenevix in the same way as chlorate of potassa, namely, by passing chlorine through an aqueous solution of baryta; but, in consequence of the similar solubility of chloride of barium and chlorate of baryta, considerable difficulty attended the separation of the products. It was effected by adding to the solution of the mixed salts, a solution of phosphate of silver in acetic acid, by which the chloride of barium was decomposed and resolved into chloride of silver and phosphate of baryta, both of which are insoluble. Chlorate of baryta may also be obtained by saturating chloric acid (obtained by the action of chlorine upon oxide of silver diffused in water) with hydrate of baryta; or it may be formed, as suggested by Mr. Wheeler, by adding a hot solution of chlorate of potassa to a solution of silicated hydrofluoric acid; the potassa is precipitated in the form of an insoluble silico-fluoride of potassium, and the chloric acid remains in solution, and may be saturated with carbonate of baryta, which throws down any excess of the silicated fluoric acid, and leaves chlorate of baryta in solution; this, when filtered and evaporated, yields prismatic crystals, soluble in about 4 parts of water at 60°, and insoluble in alcohol; they contain 1 equivalent of water. Sprinkled with sulphuric acid they become luminous. By heat they are resolved into oxygen and chloride of barium. They are decomposed by dilute sulphuric acid, furnishing sulphate of baryta and chloric acid, and are the best source of that acid. (p. 338.) The anhydrous salt consists of

							Chenevix.
Baryta	.	.	1	..	77	..	47.3
Chloric Acid	.	.	1	..	76	..	52.7
			1		153		100.0

IODIDE OF BARIUM (ba+i) is easily formed by acting upon baryta, or carbonate of baryta, by hydriodic acid, and evaporating the solution. It may also be formed by heating baryta in hydriodic gas; water and

iodide of barium are the results. It is white, very difficult of fusion, and not decomposed when heated in close vessels. Heated in the air, iodine is evolved and baryta formed. It is very soluble in water, and the solution yields small acicular crystals, which are slightly deliquescent. It consists of

Barium	.	.	1	..	69	..	35.5
Iodine	.	.	1	..	125	..	64.5
			<hr/>		<hr/>		<hr/>
			1		194		100.0

IODATE OF BARYTA ( $B+i'$ ) is a very difficultly soluble compound. It is formed by adding iodine to baryta-water: it falls in the form of a white powder, which is to be washed with distilled water. It scarcely deflagrates upon burning coals. Highly heated in the air it is resolved into oxygen, iodine, and baryta. (Gay Lussac, *Ann. de Chim.*, xci., 81.) It consists of

Baryta	.	.	1	..	77	..	31.8
Iodic Acid	.	.	1	..	165	..	68.2
			<hr/>		<hr/>		<hr/>
			1		242		100.0

BROMIDE OF BARIUM ( $ba+b$ ) is obtained by adding baryta to the ethereal solution of bromine; or by saturating hydrobromic acid with baryta and evaporating to dryness; or by boiling excess of protobromide of iron with freshly-precipitated carbonate of baryta, filtering and evaporation to dryness: it is fusible, soluble in water and in alcohol, and crystallizes in opaque mammellated masses; or, according to M. Henry, Junr., in white rhombic prisms, of a bitter taste, and consisting of

Barium	.	.	1	..	69	..	46.9
Bromine	.	.	1	..	78	..	53.1
			<hr/>		<hr/>		<hr/>
			1		147		100.0

BROMATE OF BARYTA ( $B+b'$ ) has already been mentioned as a source of bromic acid (p. 346): it forms acicular crystals, slightly soluble in cold water, and producing vivid combustion and a green flame on hot charcoal. It is obtained along with the bromide, by the action of bromine on solution of baryta. (Balard, *Ann. de Chim. et Phys.*, xxxii., 367.)

FLUORIDE OF BARIUM, ( $ba+f$ ) is best obtained, according to Berzelius, by adding fresh precipitated and moist carbonate of baryta to hydrofluoric acid; carbonic acid is expelled, and the fluoride remains in the form of a white powder, very sparingly soluble in water, but soluble in muriatic and nitric acids. It forms a double salt with chloride of barium.

NITRATE OF BARYTA ( $B+n'$ ) may be produced by dissolving the native carbonate in nitric acid, evaporating to dryness, redissolving and crystallizing; it forms permanent octoëdral and cubo-octoëdral crystals, which are anhydrous: their forms have been described by Mr. Brooke. (*Ann. of Phil.*, N. S., vii., 21.) The taste of this salt is acrid and astringent. It is soluble in 12 parts of cold and 4 of boiling water; or, according to Gay Lussac, 100 parts of water, at  $32^\circ$ , dissolve 5 parts; at  $58^\circ$ , 15.8 parts; at  $120^\circ$ , 17 parts; and at  $215^\circ$ , 35.2 parts. It is insoluble in alcohol. It is decomposed with decrepitation by a bright-red heat, furnishing pure baryta: this decomposition should be effected in

a porcelain crucible; for if platinum be used it is acted upon, and the baryta contaminated by oxide of platinum.

If a moderately-strong solution of the nitrate of baryta be added to nitric acid, a precipitation of nitrate of baryta takes place, in consequence of the insolubility of the nitrate in the acid; hence, in using nitrate of baryta as a test of the presence of sulphuric acid in nitric acid, the latter should be considerably diluted previous to its application. Nitrate of baryta is composed of

					Berzelius.	Kirwan.				
Barium	..	1	..	77	..	58.7	..	58.4	..	57
Nitric Acid	.	1	..	54	..	41.3	..	41.6	..	43
		<u>1</u>		<u>131</u>		<u>100.0</u>		<u>100.0</u>		<u>100.</u>

SULPHURET OF BARIUM ( $ba+s$ ) is formed by passing sulphuretted hydrogen over red-hot baryta in a glass tube, or by fusing a mixture of sulphur and baryta in a retort. It may also be obtained by the action of hydrogen or charcoal upon ignited sulphate of baryta. The easiest process is to mix sulphate of baryta, in fine powder, into a paste with an equal volume of flour, place it in a Hessian crucible, on which a cover is luted, and expose it to a white-heat for an hour or two, raising the temperature slowly. On pouring hot water on the ignited mass the sulphuret of barium is dissolved, and may be separated from undecomposed sulphate and excess of charcoal by filtration. (Turner.) It is readily soluble in hot water, and the solution, on cooling, deposits hydrated crystals. By exposure to air, the solution absorbs carbonic acid and oxygen, yielding carbonate and hyposulphite of baryta. It dissolves sulphur, but in what proportions has not been ascertained. When its solution is boiled with peroxide of copper till it ceases to blacken acetate of lead, and filtered whilst hot, it yields pure baryta; mixed with carbonate of potassa it yields carbonate of baryta; and, with muriatic acid, chloride of barium. It consists of

Barium	.	.	1	..	69	..	81.2
Sulphur	.	.	1	..	16	..	18.8
			<u>1</u>		<u>85</u>		<u>100.0</u>

HYPOSULPHITE OF BARYTA. ( $B+\hat{S}$ .) This salt is thrown down on pouring a solution of chloride of barium into a solution, not too dilute, of hyposulphite of lime: it is a white powder, soluble without decomposition in muriatic acid; at a low heat it takes fire, and sulphur burns off. When the solutions from which it is precipitated are dilute, it falls after some minutes, in small crystalline grains, followed by a copious separation of the salt. According to Herschel, (*Edin. Phil. Jour.* i. 20,) this salt consists of

Baryta	.	.	1	..	77	..	61.6
Hyposulphurous Acid			1	..	48	..	38.4
			<u>1</u>		<u>125</u>		<u>100.0</u>

SULPHITE OF BARYTA ( $B+\hat{S}$ ) is insoluble in water, and formed by adding sulphite of potassa to a solution of chloride of barium. It dissolves in sulphurous acid, and the solution furnishes acicular and tetraëdral crystals when very slowly evaporated. It consists of

Baryta	.	.	1	..	77	..	70.6
Sulphurous acid	.	.	1	..	32	..	29.4
			<hr/>		<hr/>		<hr/>
			1		109		100.0

**HYPOSULPHATE OF BARYTA.** ( $B + \underline{S}'$ .) When sulphurous acid gas is passed into water holding peroxide of manganese in suspension, a neutral solution is obtained, composed of sulphate and hyposulphate of manganese. These salts are decomposed by excess of baryta, and a soluble *hyposulphate of baryta* is formed, through which carbonic acid is passed, in order to saturate any excess of baryta; and the whole being heated to drive off carbonic acid, which holds a little of the carbonate in solution, the hyposulphate of baryta is obtained, and may be purified by crystallization. The solution of this salt may be decomposed by the careful addition of sulphuric acid, and the *hyposulphuric acid* is thus obtained in solution, as already stated (page 431).

The hyposulphate of baryta crystallizes in quadrangular prisms variously terminated. It dissolves, according to Gay Lussac, in 1.1 times its weight of water at  $212^{\circ}$ ; in 4.04 at  $64^{\circ}$ ; and in 7.17 at  $47^{\circ}$ . It is insoluble in alcohol. At a red-heat it gives out water and sulphurous acid, and leaves seven-tenths its weight of neutral sulphate of baryta. The crystallized salt consists of

						Welter and Gay Lussac.		Heeren.
Baryta	.	.	1	..	77	..	46.03	45.93
Hyposulphuric acid	.	.	1	..	72	..	43.41	43.31
Water	.	.	2	..	18	..	10.56	10.76
			<hr/>		<hr/>		<hr/>	<hr/>
			1		167		100.00	100.00

When a solution of this bihydrated salt is set aside in a temperature of about  $40^{\circ}$ , large four-sided prismatic crystals, terminated by four-sided pyramids, are gradually deposited, which, according to Heeren, are a *quater-hydrated hyposulphate of baryta* ( $B + \underline{S}' + 4 Q$ ), composed therefore of

						Heeren.	
Baryta	.	.	1	..	77	..	41.88
Hyposulphuric acid	.	.	1	..	72	..	39.49
Water	.	.	4	..	36	..	18.63
			<hr/>		<hr/>		<hr/>
			1		185		100.00

**SULPHATE OF BARYTA** ( $B + \underline{S}'$ ) is an abundant natural product; it is insoluble in hot and cold water, and therefore precipitates whenever sulphuric acid, or a soluble sulphate, is added to any soluble salt of baryta; hence the solutions of baryta are accurate tests of the presence of sulphuric acid, and are also used in analysis to determine its quantity. If sulphuric acid be poured upon caustic baryta, the heat is so intense as to cause ignition. If the acid be boiled upon the finely-powdered or recently-precipitated sulphate, a portion is taken up; the whole of which, however, falls again upon diluting the solution with water. The extreme insolubility of this sulphate renders the soluble salts of baryta the most delicate tests of the presence of sulphuric acid, of which a millionth part in solution may, according to Pfaff, be detected by a slight white cloud. When the sulphuric acid is in combination the test is somewhat less delicate,



but it shows the presence of 1 part of sulphate of soda in 400,000 of water. Recently-precipitated sulphate of baryta is sometimes very obstinate in subsiding from water, and will not only long remain suspended, but adheres to the glass, and will even pass through filtering-paper: heat, and a little excess of acid, generally facilitates its deposition. It may be safely heated to redness without risk of change, and hence the filter containing it, in cases of quantitative analysis, may be conveniently burned away.

Sulphate of baryta is an anhydrous compound of

					Klaproth	Berzelius.				
Baryta	.	1	..	77	..	65.8	..	66.7	..	65.643
Sulphuric acid	.	1	..	40	..	34.2	..	33.3	..	34.357
		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
		1		117		100.0		100.0		100.000

*Native Sulphate of Baryta, Heavy Spar, or Baroselenite*, is principally found in the mines of Westmoreland and Cumberland, and in Transylvania, Hungary, Saxony, and Hanover. A variety met with in Derbyshire, is called *cawk*. It occurs massive, and crystallized in a great variety of forms. Its primitive figure is a rhomboidal prism, the angles of which are  $101^{\circ} 42'$ , and  $78^{\circ} 18'$ . It is harder than carbonate of lime, but not so hard as fluor spar. Its specific gravity is 4.7.

When native sulphate of baryta is heated it decrepitates, and at a very high temperature fuses into an opaque white enamel: it was employed in the manufacture of *jasper-ware* by the late Mr. Wedgwood, and for the production of opaque white patterns and figures, upon a coloured ground. When formed into a thin cake with paste, and heated to redness, it acquires the property of phosphorescence. This was first ascertained by Vincenzo Cascariolo, of Bologna, whence the term *Bologna phosphorus* is applied to it (p. 198). The artificial sulphate of baryta is used as a pigment, under the name of *permanent white*. It is very useful for marking phials and jars in a laboratory, not being discoloured by sulphuretted hydrogen, as is the case with white lead.

As the native sulphate is a common and abundant compound, several processes have been contrived for obtaining from it pure baryta. This may be effected by reducing the crystallized sulphate to a fine powder, and heating it red-hot for half an hour in a silver crucible with three parts of carbonate of potassa: the fused mass is then boiled repeatedly in water, till it no longer affords anything soluble in that liquid; the insoluble residue, consisting chiefly of carbonate of baryta, may be digested in dilute nitric acid, by which nitrate of baryta is formed, and which will yield the pure earth by exposure to heat as above mentioned. Another method consists in exposing to a red-heat, in an earthen crucible, a mixture of six parts of finely-powdered sulphate of baryta with one of powdered charcoal, for half an hour. This converts the sulphate into sulphuret, which is to be dissolved in hot water, the solution filtered and mixed with solution of carbonate of soda as long as it occasions a precipitate, which, when washed and dried, is carbonate of baryta. Or, by adding muriatic acid to the liquid sulphuret, sulphur is thrown down, and sulphuretted hydrogen evolved, and chloride of barium formed, which may be filtered off, and if required, decomposed by carbonate of potassa. Or the sulphuret, as it comes out of the crucible, may be thrown into

*dilute* nitric acid, by which sulphuretted hydrogen is evolved, and nitrate of baryta formed, which may be separated from the remaining impurities by copious washings with hot water. When sulphate of baryta, in very fine powder, is boiled in a solution of carbonate of potassa or soda, a portion of the sulphate is also decomposed, and an equivalent proportion of carbonate of baryta formed: this decomposition of the sulphate is, however, never entire. (See page 215.)

PHOSPHURET OF BARIUM is produced by passing phosphorus over heated baryta; there is an intense action, and phosphate of baryta, together with a phosphuret of a metallic lustre, is obtained, which acts upon water, evolving phosphuretted hydrogen, and affords a solution containing *Hypophosphite of Baryta*.

HYPOPHOSPHITE OF BARYTA ( $B + \hat{p}$ ) may be obtained by the same process as hypophosphite of lime; like the other hypophosphites it is very soluble in water, and difficultly crystallizable. (Dulong, *Ann. de Chim. et Phys.*, ii., 142.)

PHOSPHITE OF BARYTA ( $B + \hat{p}$ ) was obtained by Berzelius, by adding a solution of chloride of barium to phosphite of ammonia; a crust of phosphite of baryta was formed in 24 hours. (*Ann. de Chim. et Phys.*, ii., 231.) A red-heat converts it into neutral phosphate of baryta. It dissolves in phosphorous acid, forming, apparently, a distinct *biphosphite of baryta*. It consists of

					Berzelius.
Baryta	.	. 1	.. 77	.. 67.5	.. 67.24
Phosphorous acid	.	. 1	.. 28	.. 24.5	.. 24.31
Water	.	. 1	.. 9	.. 8.0	.. 8.45
		1	114	100.0	100.00

PHOSPHATE OF BARYTA. ( $B + p'$ .) When a solution of neutral phosphate of ammonia is dropped (not in excess) into a neutral barytic solution, an insoluble white powder falls, which melts into a gray enamel when strongly heated, and is soluble in muriatic, nitric, and phosphoric acid. It consists of

					Berzelius.
Baryta	.	. 1	.. 77	.. 68.1	.. 68.2
Phosphoric acid	.	. 1	.. 36	.. 31.9	.. 31.8
		1	113	100.0	100.0

SESQUIPHOSPHATE OF BARYTA. When a saturated solution of phosphate of baryta in phosphoric acid is mixed with alcohol, a bulky precipitate falls, which, when dried, forms a light, white, tasteless, powder; composed of

					Berzelius.
Baryta	.	. 1	.. 77	.. 58.7	.. 60.87
Phosphoric acid	.	. $1\frac{1}{2}$	.. 54	.. 41.3	.. 39.13
		1	131	100.0	100.00

BIPHOSPHATE OF BARYTA. Biphosphate of soda occasions no precipitate in solution of chloride of barium. When a saturated solution of neutral phosphate of baryta in phosphoric acid is carefully evaporated, it yields crystals, which, after having been dried on filtering-paper, are permanent in the air. Water resolves them into phosphoric acid and neutral

phosphate. (Berzelius, *Ann. de Chim. et Phys.*, ii. and xi.) At a red-heat they lose water of crystallization, and a white spongy mass is formed. The crystals of this salt contain two proportionals of water; in its anhydrous state, it consists of

						Berzelius.
Baryta . . . . .	1	..	77	..	51.7	.. 52.2
Phosphoric acid . . . . .	2	..	72	..	48.3	.. 47.8
	1		149		100.0	100.0

Berzelius found, on digesting neutral phosphate of baryta in ammonia, that a portion of the acid was abstracted, leaving a definite combination of one proportional and a quarter of baryta, with  $\frac{1}{4}$  of acid.

SELENITE OF BARYTA falls in the form of a white insoluble powder, when solution of selenite of potassa is added to muriate of baryta. *Biselenite of baryta* is formed by dissolving carbonate of baryta in selenious acid; it forms a granular crystalline powder very difficultly soluble in water

SELENIATE OF BARYTA resembles the sulphate in insolubility.

CARBONATE OF BARYTA. (B + *car'*.) This salt falls in the form of a white powder, when the soluble salts of baryta are precipitated by the alkaline carbonates. It is so nearly insoluble, that water at 60° only takes up about  $\frac{1}{4300}$ , and at 212° about  $\frac{1}{2300}$  th part. Water saturated with carbonic acid dissolves  $\frac{1}{830}$ . It has no action on vegetable colours: it is highly poisonous. When *baryta-water* is added to solutions of the carbonated alkalis, it abstracts their carbonic acid. Like the other carbonates, it is decomposed by the stronger acids with effervescence. It consists of

						Withering.	Berzelius.
Baryta . . . . .	1	..	77	..	77.7	.. 78.6	.. 77.9
Carbonic acid . . . . .	1	..	22	..	22.3	.. 21.4	.. 22.1
	1		99		100.0	100.0	100.0

*Native Carbonate of Baryta* was first discovered at Anglesark, in Lancashire, by Dr. Withering, and hence acquired the name of *Witherite*. It has also been found in Wales, Cumberland, Durham, Westmoreland, and Shropshire. Its primitive crystal is an obtuse rhomboid: sometimes it forms pyramidal six-sided prisms. That found in Lancashire is in globular masses of a radiated structure. It is useful as a source of pure baryta and its salts, and though scarcely soluble in water, is poisonous. It dissolves very sparingly in solution of carbonic acid, whence the superiority of baryta-water to lime-water, in some cases, as a test of carbonic acid. The native carbonate of baryta is much more difficult of decomposition by heat than the artificial; but if mixed with a little charcoal-powder, and kept for some time in a red-heat, carbonic oxide escapes, and pure baryta is formed.

CYANURET OF BARIUM (*ba + cy*) is precipitated in the form of a white powder when hydrocyanic acid is mixed with baryta-water. It is also formed by heating ferrocyanuret of barium in a retort, for it is not decomposed at a temperature which destroys the cyanuret of iron: it is sparingly soluble in water, and the solution soon becomes covered by a film of carbonate of baryta, when in contact with air.

**CYANATE OF BARYTA.** ( $B + cy'$ .) When cyanogen is passed through a mixture of hydrate of baryta and water, cyanate of baryta and cyanuret of barium are formed: the latter may be decomposed by a stream of carbonic acid: the filtered liquor then yields, when concentrated by evaporation and mixed with alcohol, small prismatic crystals: when their aqueous solution is evaporated, it decomposes into carbonate of baryta and ammonia.

**SULPHOCYANURET OF BARIUM** is formed by heating the ferrocyanuret with sulphur: it is soluble in water, and forms brilliant acicular crystals, which are slightly deliquescent.

**BORATE OF BARYTA** is formed by mixing a soluble salt of baryta with a solution of borax, and fusing the washed precipitate: it is a gray transparent glass, very sparingly soluble in water; before fusion it is a *hydrated salt*, somewhat more soluble in water, and its solution, according to Berzelius, is decomposed by carbonic acid. It is composed of

						Thenard.	Berzelius.	L. Gmelin.	
Baryta . . .	1	. .	77	. .	53	. .	57.8	. .	54.9
Boracic acid .	1	. .	68	. .	47	. .	42.2	. .	45.1
	1		145		100		100.0		100.0

**BOROFLUORIDE OF BARIUM.** Carbonate of baryta is added to the aqueous solution of fluoboracic acid, as long as it is dissolved: on evaporation some boracic acid first separates, and afterwards prismatic crystals of the borofluoride, soluble in water without decomposition, and deliquescent in damp air: they contain 10.34 *per cent.* of water: they are decomposed at a red-heat; liquid fluoboric acid first passes off, then fluoboric gas; and fluoride of barium remains\*.

**PROPERTIES OF BARYTIC SALTS.** The soluble barytic salts furnish white precipitates of carbonate and sulphate of baryta, upon the addition of carbonate or sulphate of soda. They give a yellow tinge to the flame of spirit of wine. The sulphate is insoluble in nitric acid and in the alkalis, and very sparingly soluble in sulphuric acid. Nearly all the barytic compounds are poisonous. Sulphate of baryta is, however, harmless; the safest antidote, therefore, is solution of sulphate of soda. (Orfila, *Traité de Poisons*; Christison *on Poisons*.) Chloride of barium has been employed in medicine, but the principal use of baryta is in the chemical laboratory. It is possible that pure baryta might be economically used for the decomposition of sulphate of soda, to obtain the pure alkali.

## § VI. STRONTIUM.

*Strontia* (or strontites) was first discovered in the state of *carbonate* at Strontian in Argyleshire, and was supposed to be a carbonate of baryta.

\* The only compound mineral hitherto discovered containing baryta, is the *har-motome* or *cross-stone*; in that from Andreasberg, Klaproth found

Silica	.	.	.	.		49
Alumina	.	.	.	.		16
Baryta	.	.	.	.		18
Water.	.	.	.	.		15
						98

Crawford, in 1790, pointed out some of its distinctive characters, but it was first shown to contain a peculiar earth by Dr. Hope, in 1792, (*Edin. Phil. Trans.*, iv.,) and by Klaproth in 1793, (*Crell's Annals*, 1793 and 1794.) It is a substance of rare occurrence. The existence of *strontium*, as the metallic base of the earth *strontia*, was first demonstrated by Davy in 1808. It is probably as heavy as barium, and resembles it in appearance and in its leading chemical characters; it has, however, been as yet very imperfectly examined. The equivalent of strontium deduced from the best analyses of its compounds is 44, (43.8 Turner, 44 Gmelin.)

PROTOXIDE OF STRONTIUM; STRONTIA. (*str* + *o*) or STR. Strontium is rapidly oxidized by exposure to air, and it decomposes water, evolving hydrogen, and forming the oxide. Strontia may be obtained from the nitrate, the carbonate, and the sulphate of strontia, by processes similar to those directed in regard to baryta, (p. 606.) It is a grayish-white substance; its specific gravity is between 3 and 4; it is extremely infusible, not volatile, has an acrid taste, and an alkaline reaction upon vegetable colours: it is less caustic than the fixed alkalis and baryta. It consists of

				Strömeyer.	Davy.	Berzelius.
Strontium	. 1	.. 44	.. 84.6	.. 84.67	.. 86	.. 84.55
Oxygen	. . 1	.. 8	.. 15.4	.. 15.33	.. 14	.. 15.45
	<u>1</u>	<u>52</u>	<u>100.0</u>	<u>100.00</u>	<u>100</u>	<u>100.00</u>

HYDRATE OF STRONTIA. (*STR* + *q*.) When strontia is sprinkled with water it heats and falls to powder like baryta, forming a solid hydrated compound of 1 equivalent of strontia = 52, and 1 of water = 9; it fuses, but does not part with its water, at a red-heat. It is insoluble in alcohol. It dissolves in about 160 parts of water at 60°, forming *strontia-water*. Boiling water dissolves it more abundantly, and on cooling deposits crystals in the form of thin quadrangular tables: their primary form is a right square prism (Brooke, *Ann. of Phil.* 2nd series, vii. 287,) they are soluble in 50 parts of cold and 2 of boiling water (Dalton,) and are converted by heat into the protohydrate. They contain according to Phillips (*Phil. Mag.* 3rd series, vi. 52) 63.76 *per cent.* of water, and consist, therefore, of 1 equivalent of strontia = 52, and 10 equivalents of water = 90.

PEROXIDE OF STRONTIUM may probably be formed by passing oxygen over heated strontia, but it has not, I believe, hitherto been so obtained. When peroxide of hydrogen is mixed with strontia-water, brilliant crystalline scales are thrown down, composed according to Thenard of 1 equivalent of strontium and 2 of oxygen. (*str* + <sub>2</sub> *o*.)

CHLORIDE OF STRONTIUM. (*str* + *c*.) When strontia is heated in chlorine, it evolves 1 volume of oxygen for every 2 volumes of chlorine that are absorbed, and a chloride of strontium is the result. Heated in muriatic acid, strontia absorbs the gas with ignition and evolution of water. Chloride of strontium is generally obtained by dissolving *carbonate of strontia* in muriatic acid, evaporating to dryness, and fusing the residue. It is of a gray colour and an acrid taste. It dissolves in alcohol, and the solution burns with a purple-coloured flame. Its aqueous solution furnishes, upon evaporation, hexagonal prismatic crystals, which are

deliquescent and soluble in two parts of water at 60°. They contain 40.5 per cent. of water of crystallization. (Berzelius.) The anhydrous or fused chloride consists of

							Davy.
Strontium . . .	1	..	44	..	55	..	58
Chlorine . . .	1	..	36	..	45	..	42
	1		80		100		100

CHLORATE OF STRONTIA, (STR + C'), is obtained in the same way as the chlorate of baryta; it is a very soluble and deliquescent salt, difficultly crystallizable, and detonates when thrown upon red-hot coals with a beautiful purple light. It dissolves in alcohol.

IODIDE OF STRONTIUM, (STR + I,) may be formed as iodide of barium. Dissolved in water, and carefully evaporated, it furnishes delicate prismatic crystals (*Hydriodate of Strontia*), which, heated in close vessels, fuse without decomposition; heated in the open air, iodine escapes, and strontia is generated. Iodide of strontium consists of

Strontium . . .	1	..	44	..	26.1
Iodine . . .	1	..	125	..	73.9
	1		169		100.0

IODATE OF STRONTIA, (STR + I'), is obtained as iodate of baryta; it is soluble in 4 parts of cold water, and is resolved at a red heat into oxygen, iodine, and strontia.

BROMIDE OF STRONTIUM AND BROMATE OF STRONTIA have not been examined.

FLUORIDE OF STRONTIUM is a very difficultly soluble white powder, obtained in the same way as fluoride of barium.

NITRATE OF STRONTIA. (STR + N'.) This salt is obtained by the same process as *nitrate of baryta*: it crystallizes in octoëdrons: it is soluble in 5 parts of water at 60°, and in half its weight of boiling water. It is insoluble in anhydrous alcohol. Its taste is pungent and cooling. At a red-heat the acid is evolved and decomposed, and strontia remains. According to Stromeyer, the crystallized salt, as ordinarily prepared, contains no water of crystallization. It is used in the *red fire* employed at the theatres, which consists of 40 parts of dry nitrate of strontia, 13 of powdered sulphur, 5 of chlorate of potassa, and 4 of sulphuret of antimony. The chlorate and sulphuret should be separately powdered, and mixed together on paper with the other ingredients; a very small quantity of powdered charcoal may also be added. When nitrate of strontia is finely powdered and mixed with spirit of wine, it communicates a beautiful red tint to its flame. It is composed of

Strontia . . .	1	..	52	..	49	..	49.38
Nitric acid . .	1	..	54	..	51	..	50.62
	1		106		100		100.00
							100.00
							100.0

HYDRATED NITRATE OF STRONTIA. (STR + N' + 4 Q.) When a moderately-strong solution of the above *anhydrous nitrate* is set aside, it sometimes deposits *oblique rhombic crystals*, (Brooke, *Ann. of Phil.*, 2nd series, vii., 288,) composed of

Strontia . . .	1	..	52	..	36.6
Nitric acid . .	1	..	54	..	38.0
Water . . .	4	..	36	..	25.4
	<hr/>		<hr/>		<hr/>
	1		142		100.0

SULPHURET OF STRONTIUM, (*str* + *S*.) may be formed by fusing strontia and sulphur in a green-glass tube; or by exposing the powdered sulphate to a red-heat with charcoal. It dissolves in water with the same phenomena as sulphuret of barium, and its solution furnishes, by cautious evaporation, crystals of *hydrosulphuret of strontia*. When strontia or sulphuret of strontium is dissolved in water by a current of sulphuretted hydrogen, and the solution evaporated in vacuo, square prismatic crystals are obtained, which, when heated, fuse and give off water and sulphuretted hydrogen, sulphuret of strontium remaining in the form of a white powder. (Berzelius.)

HYPOSULPHITE OF STRONTIA, (*STR* + *S̄*.) is formed by passing sulphurous acid into the solution of the sulphuret, or by exposing it to air: it crystallizes in rhomboids permanent at common temperatures, and soluble in about 5 parts of water at 60°. (Gay Lussac, *Ann. de Chim.*, lxxxv.) According to Herschel, this salt is doubly refractive. Its taste is bitter, and it is insoluble in alcohol. The crystals consist of

					Gay Lussac.
Strontia . . .	1	..	52	..	35.8
Hyposulphurous acid .	1	..	48	..	33.1
Water . . .	5	..	45	..	31.1
	<hr/>		<hr/>		<hr/>
	1		145		100.0

SULPHITE OF STRONTIA, (*STR* + *S̄*.) is tasteless, nearly insoluble, and becomes *sulphate* by exposure to air.

HYPOSULPHATE OF STRONTIA, (*STR* + *S'*.) crystallizes in hexangular tables, soluble in 4.5 water at 60°, and in 1.5 at 212°; insoluble in alcohol: bitter, permanent, and leaving 0.577 of *sulphate* of strontia after heating to redness. They consist of

					Heeren.
Strontia . . .	1	..	52	..	32.54
Hyposulphuric acid	1	..	72	..	45.36
Water . . .	4	..	36	..	22.10
	<hr/>		<hr/>		<hr/>
	1		160		100.00

SULPHATE OF STRONTIA. (*STR* + *S'*.) It is nearly insoluble, 1 part requiring 3840 of hot, and 4000 of cold water, for its solution; it is therefore thrown down whenever sulphuric acid or soluble sulphates are added to solutions of strontia. When heated with charcoal, its acid is decomposed, and *sulphuret of strontium* is formed, which affords nitrate by the action of nitric acid. This process, as practised upon sulphate of baryta, is sometimes adopted to obtain the earth. Sulphate of strontia dissolves in hot sulphuric acid, but is thrown down upon adding water. At a very high heat it fuses into an opaque enamel. According to Moretti, its acid is expelled at a red heat by arsenic acid. It consists of

					Vauquelin.	Stromeyer.	Klaproth.				
Strontia . . .	1	..	52	..	56.52	..	54	..	57	..	58
Sulphuric acid .	1	..	40	..	43.48	..	46	..	43	..	42
	<u>1</u>		<u>92</u>		<u>100.00</u>		<u>100</u>		<u>100</u>		<u>100</u>

*Native Sulphate of Strontia* is sometimes of a blue tint, and has hence been called *celestine*. Sometimes it is colourless and transparent. Its primitive form is a prism of  $104^{\circ} 48'$  and  $75^{\circ} 42'$  with a rhomboidal basis. It has been found at Strontian in Argyleshire; in the vicinity of Bristol; at Montmartre near Paris; in Germany, America, &c. The finest crystallized specimens are accompanied with native sulphur, from Sicily. Its specific gravity is 3.2. *A baryto-sulphate of strontia*, composed of about 3 atoms of sulphate of baryta and 7 of sulphate of strontia, is found in Upper Canada; and another variety, called *radiated celestine*, occurs at Nörden, near Hanover.

PHOSPHURET OF STRONTIUM, (*str* + *p*,) has properties analogous to those of phosphuret of barium.

HYPOPHOSPHITE OF STRONTIA has been examined by Dulong: it is a very soluble and difficultly-crystallizable salt, and is obtained by a process similar to that for forming the hypophosphite of baryta. (*Ann. de Chim. et Phys.*, ii., 142.)

PHOSPHITE OF STRONTIA. When carbonate of strontia is dissolved in phosphorous acid, a crystallized salt is obtained on evaporation: the crystals are decomposed by warm water, and a white powder falls, which is probably a neutral phosphite. (Berzelius.) When solutions of chloride of strontium and chloride of phosphorus are mixed and exposed to spontaneous evaporation, crystals of phosphite of strontia are deposited: when they are heated, phosphuretted hydrogen is evolved, and phosphate of strontia formed.

PHOSPHATE OF STRONTIA (*STR* + *p'*) is an insoluble white salt; it is soluble in excess of phosphoric acid. It is entirely decomposed by sulphuric acid. By igniting it with charcoal, *phosphuret of strontium* is obtained. It fuses, before the blowpipe, into a white enamel. Obtained by precipitation from nitrate of strontia, by neutral phosphate of soda, it consists of

					Vauquelin.	Stromeyer.			
Strontia . . .	1	..	52	..	59.1	..	58.76	..	63.435
Phosphoric acid	1	..	36	..	40.9	..	41.24	..	36.565
	<u>1</u>		<u>88</u>		<u>100.0</u>		<u>100.00</u>		<u>100.000</u>

SELENITE OF STRONTIA is an insoluble white powder. (Berzelius, *Ann. de Chim. et Phys.*, ix., 263.)

CARBONATE OF STRONTIA, (*STR* + *car'*,) when artificially formed, is a white powder, soluble in 1536 parts of hot water. When strongly heated with a little charcoal-powder, it is decomposed, carbonic oxide is given off, and pure strontia remains; but it is not decomposed by heat alone. When steam is passed over it at a high temperature, it parts with its acid and becomes a hydrate. Before the oxyhydrogen blowpipe it slowly volatilizes with a red light. It is very slightly soluble by excess of carbonic acid, and the solution deposits small acicular crystals. It is composed of



					Stromeyer.	Ure.	Klaproth.
Strontia . . .	1	52	70.3	70.313	69.8	69.5	
Carbonic acid	1	22	29.7	29.687	30.2	30.5	
	1	74	100.0	100.000	100.0	100.0	

*Native Carbonate of Strontia* or *Strontianite* is a rare mineral. It has a greenish tint, and occurs in radiated masses, and sometimes in acicular and hexaëdral crystals. It was first discovered, in 1787, at Strontian in Argyleshire, whence the name of this earth; it has also been found in Saxony, and in Peru. Its specific gravity is 3.6. It generally contains traces of carbonate of lime.

CYANURET OF STRONTIUM has not been examined.

SULPHOCYANATE OF STRONTIA forms delicate prismatic crystals, which deliquesce on exposure.

BORATE OF STRONTIA was formed by Dr. Hope. It is a white powder soluble in 130 parts of water.

PROPERTIES OF THE SALTS OF STRONTIA. There is in many respects a resemblance between strontia and baryta, which has led to confusion in analysis. They are both found native in the states of sulphate and carbonate only; both sulphates are slightly soluble in excess of sulphuric acid, and nearly insoluble in water; they are decomposable by similar means, as well as the native carbonates; they are both crystallizable from their hot aqueous solutions, and both attract carbonic acid. The carbonates are each soluble with effervescence in most of the acids; but the native carbonates are not so easily acted on as the artificial. Pure ammonia precipitates neither one nor the other. The following are essential distinctions. Baryta and all its salts, except the sulphate, are poisonous. The corresponding strontitic salts are not so. Baryta tinges flame yellow; strontia, red. Strontia has less attraction for acids than baryta; hence the strontitic salts are decomposed by baryta. The greater number of the barytic salts are less soluble than those of strontia, and they differ in their respective forms and solubilities. Pure baryta is ten times more soluble in water than pure strontia. Baryta and Strontia may also be distinguished from each other by the following process: Dissolve the earth in muriatic, nitric, or any other acid with which it forms a soluble salt, then add excess of solution of sulphate of soda, filter, and test the clear fluid by carbonate of potassa: if any precipitate falls, the earth was strontia; if none, baryta. This shows the slight solubility of sulphate of strontia, and the insolubility (in such solution) of sulphate of baryta; but it is doubtful whether, in such cases, lime has not sometimes been present. Succinate of ammonia, and fluosilicic acid, precipitate baryta, but not strontia.

## § VII. MAGNESIUM.

SIR H. DAVY found that when moistened magnesia is negatively electrized with mercury, the resulting amalgam decomposes water, and gives rise to the formation of *magnesia*. The metallic base of magnesia had not, however, been examined, till Bussy, in 1830, obtained it by the decomposition of *chloride of magnesium* by potassium. (*Ann. de Chim.*

*et Phys.*, xlvi.) To effect this, some globules of potassium are put into a glass tube, and fragments of the chloride placed over them: the latter is then heated till it begins to fuse, and the potassium allowed to run through it by slightly inclining the tube; light is evolved, and the mass, when cold, affords, on washing with water, a number of small metallic globules, of a silver colour and lustre, and hard but malleable. They are not acted upon by water. Mixed with chloride of potassium and fused, they coalesce into one mass, their fusing-point being apparently about that of silver. They dissolve in dilute muriatic, nitric, sulphuric, and acetic acids, and furnish solutions of magnesia. Heated in the air, or in oxygen, they burn vividly into magnesia. The equivalent of magnesium may be assumed as 12, (12.7 Turner, 12 Gmelin.)

OXIDE OF MAGNESIUM; MAGNESIA. (*mag* + *o*.) This is the only compound of magnesium and oxygen; it is generally procured by exposing the carbonate of magnesia for some time to a red-heat. Magnesia is a white insipid substance, which slightly greens the blue of violets, and reddens turmeric. But water which has been agitated with magnesia, when filtered through paper, does not produce similar effects (Henry.) Its specific gravity is 2.3; it is almost infusible, and nearly insoluble in water. Cold water is said to dissolve it in the proportion of between a six and seven thousandth part; whereas one part of the earth, according to Dr. Fyfe, requires for its solution 36000 of boiling water. I once succeeded in agglutinating a small portion of this earth in the Voltaic flame, and whilst exposed to this high temperature, it was perfectly fused by directing upon it the flame of oxygen and hydrogen. A mixture of magnesia and lime is scarcely more fusible than the pure earth. It does not absorb carbonic acid or moisture, nearly so rapidly as the other alkaline earths, and scarcely any heat is produced by pouring water upon it. When thrown down from its solutions by potassa, collected upon a filter, and dried at  $212^{\circ}$ , it still retains a considerable quantity of water, amounting to about one-fourth its weight; in this state, therefore, it is a *hydrate of magnesia*. It is insoluble in solutions of potassa and soda. It forms bitter saline compounds with the acids, and is most readily distinguished from the other earths by the solubility and bitter taste of its *sulphate*: the sulphates of the other alkaline earths being tasteless, or very difficultly soluble, while those of the earths proper are sweet or astringent. The attractions of magnesia for the acids correspond, in most instances, closely with those of ammonia, which is in some cases displaced by, and in others, displaces magnesia. It may also be observed, that ammonia and magnesia produce double salts with most of the acids. Magnesia consists of

						Wollaston.	Gay Lussac.	Berzelius.				
Magnesium	1	..	12	..	60	..	59.3	..	59.5	..	61.29	
Oxygen	.	1	..	8	..	40	..	40.7	..	40.5	..	38.71
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		1		20		100		100.0		100.0		100.00

*Native Hydrate of Magnesia.* This mineral was first discovered by Dr. Bruce, in the serpentine rocks of Hoboken, in New Jersey; it has also been found by Dr. Hibbert, in a vein, traversing serpentine, at Swina-

ness in Unst, one of the Shetland Isles. It has a greenish hue, and a soft lamellar texture. It consists of

Magnesia	1	..	20	..	69	..	Bruce. 70	..	Fyfe 69.75	..	Stromeyer. 68.35
Water	1	..	9	..	31	..	30	..	30.25	..	30.90
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	1		29		100.		100		100.00		99.15

CHLORIDE OF MAGNESIUM, (*mag* + *c*.) may be obtained by passing chlorine over red-hot magnesia, mixed with a little charcoal; or more conveniently, by heating in a retort a mixture of 1 part of magnesia with 2 of sal-ammoniac; or by Liebig's method, which consists in evaporating a solution of equal parts of the muriates of ammonia and of magnesia, and heating the dry residue in a platinum vessel till the muriate of ammonia is expelled and the mass fuses. The residuary *chloride of magnesium* forms a lamellar white crystalline mass, which evolves heat when acted on by water. This chloride cannot be obtained by merely evaporating its aqueous solution to dryness in an open vessel, for in that case muriatic acid escapes, and magnesia remains; but Davy found that magnesia heated in chlorine absorbed it, and gave out the usual proportion of oxygen. Chloride of magnesium consists of

Magnesium	. .	1	..	12	..	25
Chlorine	. . .	1	..	36	..	75
		<hr/>				<hr/>
		1		48		100

When solution of chloride of magnesium is concentrated by evaporation, and exposed to a cold atmosphere, it yields prismatic hydrated crystals, deliquescent, very soluble in water and alcohol, and of a bitter and biting taste: they contain, according to Murray, 5, according to Thomson, 6 equivalents of water. This salt is generally termed *muriate of magnesia*; it is found in a few saline springs, and in the water of the ocean. By evaporating a pint of *sea-water* we obtain

Common salt	180.5 grs.
Chloride of magnesium	23
Sulphate of magnesia	15.5
„ lime	7.1
	<hr/>
	226.1

According to Murray (*Edin. Phil. Trans.* viii. 205,) the elements of these salts, *previous to evaporation* are arranged thus:—

Common salt	180.5 grs.
Muriate of magnesia	18.3
„ lime	5.7
Sulphate of magnesia	21.6
	<hr/>
	226.1

The average specific gravity of *sea-water* is 1.026 or 1.028. It freezes at about 28.5°, and does not appear materially to differ in composition in different latitudes, provided it be taken from a sufficient depth. Near the mouths of rivers, and in the vicinities of melting ice or snow, its composition will of course vary. Traces of chloride of potassium, and of

iodine and bromine, may also be found in it; and, according to Dr. Marcet (*Phil. Trans.*, 1822), of triple sulphate of magnesia and potassa, and of muriate of ammonia. He has also detected in it a minute portion of carbonate of lime.

**CHLORIDE OF MAGNESIA.** The fluid obtained by condensing chlorine in a mixture of magnesia and water, was recommended by Davy (*Elements of Chem. Phil.*, 243) for some delicate bleaching-operations, but it has not been generally employed.

**CHLORATE OF MAGNESIA** is obtained by mixing a solution of fluosilicate of magnesia with a hot saturated solution of chlorate of potassa, as long as a precipitate falls. (Berzelius.) This salt has not been examined.

**AMMONIO-CHLORIDE OF MAGNESIUM** is a crystallizable salt soluble in 6 parts of water, at 60°.

**POTASSO-CHLORIDE OF MAGNESIUM** may, by very careful evaporation, be obtained in rhombic crystals; but the constitution of this salt is so delicate, that it is liable to be separated into chloride of potassium and of magnesium by water alone; and it is with certainty decomposed by alcohol, which takes up the magnesian chloride, and leaves the other undissolved (Marcet, *Phil. Trans.*, 1822, p. 456.)

**IODIDE OF MAGNESIUM.** (*mag + i.*) When iodine is heated with magnesia and water, *iodide of Magnesium* and *iodate of magnesia* are formed. By concentrating the solution, both salts are partly decomposed, and a brown flocculent iodide of magnesia falls (resembling kermes in appearance,) which, when heated, loses part of its iodine, and is changed into a *subiodide*. (Henry, i. 593.) The hydrated iodide is very difficultly crystallized, and when heated, gives off hydriodic acid and leaves magnesia.

**BROMIDE OF MAGNESIUM,** (*mag + b.*) is only known as a deliquescent *hydrate*, resolved, by heat and air, into magnesia and hydrobromic acid.

**FLUORIDE OF MAGNESIUM** (*mag + f.*) is obtained by digesting magnesia in hydrofluoric acid. Berzelius says that it is insoluble, and undecomposed at a red-heat.

**NITRATE OF MAGNESIA** ( $M + n'$ ) crystallizes with difficulty in rhomboidal prisms, deliquescent, and soluble in its weight of water. In pure alcohol it is nearly insoluble, but 1 part dissolves in about 9 of alcohol of the specific gravity, 840. Its taste is cooling and bitter, and it is decomposed at a red-heat. It is sometimes found in crude nitre. The crystallized salt, according to Kirwan and Bergman, contains about 30 per cent. of water; according to Thomson 6 atoms: anhydrous nitrate of magnesia consists of

Magnesia	.	1	..	20	..	27	..	28	..	30.4
Nitric acid	.	1	..	54	..	73	..	72	..	69.6
		<u>1</u>		<u>74</u>		<u>100</u>		<u>100</u>		<u>100.0</u>

**AMMONIO-NITRATE OF MAGNESIA** may be obtained by evaporating a mixed solution of nitrate of ammonia and nitrate of magnesia; it forms prismatic crystals, of a bitter acrid taste, soluble in about 11 parts of water at 60°, and less deliquescent than their component salts separately. (FOURCROY, *Ann. de Chim.* iv. 215.)

SULPHURET OF MAGNESIUM. (*mag* + *S*.) Sulphur and magnesia do not appear to form a complete sulphuret, for when melted together the compound does not dissolve in water; and when heated, the sulphur burns off. Nor can a sulphuret of magnesia be obtained by heating the metal with sulphur. Berzelius states that sulphate of magnesia decomposed by an aqueous solution of sulphuret of barium yields a precipitate of sulphate of baryta and a solution of sulphuret of magnesia.

HYPOSULPHITE OF MAGNESIA ( $M + \underline{S}$ ) may be formed by boiling flowers of sulphur in solution of sulphite of magnesia; it is bitter, very soluble, but not deliquescent. Being more soluble in hot than cold water, it readily crystallizes as its solution cools; heated, sulphur escapes, but it is not very combustible.

SULPHITE OF MAGNESIA ( $M + \underline{S}$ ) is prepared by passing sulphurous acid through water containing diffused magnesia. It forms tetraëdral crystals soluble in 20 parts of water at 60°.

AMMONIO-SULPHITE OF MAGNESIA may be obtained by mixing the solution of the two salts, or by saturating acid sulphite of magnesia, with ammonia. It forms transparent, difficultly-soluble crystals.

HYPOSULPHATE OF MAGNESIA ( $M + \underline{S}'$ ) is difficultly crystallizable and readily soluble in water, but not deliquescent. It is formed by mixing the solutions of sulphate of magnesia and hyposulphate of baryta, and appears from Heeren's analysis, (Poggendorff, vii. 179,) to consist, when crystallized, of

Magnesia . . . .	1	..	20	..	13.70
Hyposulphuric acid . . . .	1	..	72	..	49.31
Water . . . .	6	..	54	..	36.99
	1		146		100.00

SULPHATE OF MAGNESIA ( $M + S'$ ) is a commonly-occurring compound of this earth, much used in medicine as an aperient. When concentrated sulphuric acid is poured upon magnesia, intense heat is produced, and sometimes light. If the acid be dilute, and poured upon carbonate of magnesia, the latter is slowly dissolved with effervescence; and, upon evaporating the filtered solution, crystals of sulphate of magnesia may be obtained. Sulphate of magnesia is largely consumed for the medicinal preparation of carbonate of magnesia. It crystallizes (see fig. 10) in four-sided prisms with reversed diëdral summits, or four-sided pyramids. (Brooke, *Ann. of Phil.*, 2nd. series, vi. 40.) Exposed to the air, it has, when pure, a slight tendency to efflorescence, but the salt of commerce is often deliquescent from the presence of a little chloride of magnesium. Its taste is saline and bitter. It is soluble in its own weight of water at 60°, and in three-fourths its weight of boiling water. When exposed to a red-heat, it loses its water of crystallization, but is not decomposed. At a high temperature it runs into a white enamel.

The aqueous solution of sulphate of magnesia furnishes a precipitate of hydrated carbonate upon the addition of the carbonates of potassa and soda, but carbonate of ammonia does not even render it turbid, unless heat be applied, in which case a precipitate is also thrown down. The alkaline bicarbonates occasion no precipitate when added to cold solution of sulphate of magnesia, but after some hours crystals of hydrated carbonate of magnesia are deposited.

This salt is usually obtained from sea-water, the residue of which, after the separation of common salt, is known by the name of *bittern*, and contains sulphate and chloride of magnesium; the latter is decomposed by sulphuric acid: it is also occasionally obtained from saline springs; and sometimes by the action of sulphuric acid on magnesian limestone. It is also largely obtained in some alum-works; but the crystallized salt from those sources generally contains traces of iron, which renders it unfit for many of the purposes of the pharmaceutical laboratory. It was once procured from the springs of Epsom in Surrey, and hence called *Epsom salt*. It has been found *native*, constituting the *bitter salt* and *hair salt* of mineralogists: it not unfrequently occurs as a fine capillary incrustation upon the damp walls of cellars and new buildings.

The sulphate of magnesia of commerce is occasionally adulterated with small crystals of sulphate of soda; the fraud is detected by the inferior weight of the precipitate, occasioned by adding carbonate of potassa; 100 grains of pure crystallized sulphate of magnesia furnishing a precipitate weighing, when dried at  $212^{\circ}$ , about 40 grains. Anhydrous sulphate of magnesia consists of

					Henry.	Gay Lussac.	Berzelius.	Wenzel.					
Magnesia .	1	..	20	..	33.33	..	32.14	..	33	..	34	..	35.5
Sulphuric acid	1	..	40	..	66.67	..	67.86	..	67	..	66	..	64.5
	<u>1</u>		<u>60</u>		<u>100.00</u>		<u>100.00</u>		<u>100</u>		<u>100</u>		<u>100.0</u>

And the *crystallized* salt consists of

						Gay Lussac.	Wenzel.		
Magnesia .	1	..	20	..	16.26	..	16.04	..	16.86
Sulphuric acid	1	..	40	..	32.52	..	32.53	..	30.64
Water .	7	..	63	..	51.22	..	51.43	..	52.50
	<u>1</u>		<u>123</u>		<u>100.00</u>		<u>100.00</u>		<u>100.00</u>

AMMONIO-SULPHATE OF MAGNESIA may be obtained by mixing solution of sulphate of ammonia with solution of sulphate of magnesia; or by pouring ammonia into a solution of the sulphate of magnesia, in which case, part only of the magnesia is thrown down, the remainder forming, with the sulphate of ammonia, this triple salt. It crystallizes in oblique rhombic prisms, (Brooke, *Ann. of Phil.*, 2nd. series, vii. 117,) consisting of

				Mitscherlich.		Fourcroy.	
Ammonia .	1	..	17	..	9.00	Sulphate of } Ammonia. }	.. 32
Magnesia .	1	..	20	..	10.58		
Sulphuric acid	2	..	80	..	42.33	Sulphate of } Magnesia. }	.. 68
Water . .	8	..	72	..	38.09		
Crystallized . .	<u>1</u>		<u>189</u>		<u>100.00</u>	Dry . . .	<u>100</u>

SULPHATE OF POTASSA AND MAGNESIA ( $P + M + 2S'$ ) forms rhomboidal crystals, scarcely more soluble than sulphate of potassa, and of a bitter taste. This salt appears, from Dr. Marcet's observations, to exist in sea-water. It may be obtained by evaporating a mixture of 2 parts of sulphate of potassa, and 1 of sulphate of magnesia, in complex crystals consisting of

				Mitscherlich.	
Potassa	.	.	1	48	23.46
Magnesia	.	.	1	20	9.94
Sulphuric acid	.	.	2	80	39.76
Water	.	.	6	54	26.84
			—	—	—
			1	202	100.00

SULPHATE OF SODA AND MAGNESIA, (S + M + 2S') forms truncated rhombic crystals, soluble in about 3 parts of water at 60°; it was first examined by Link, and afterwards by Dr. Murray, (*Edin. Phil. Trans.*, viii.) The crystals contain

				Murray.		
Sulphate of soda	.	.	1	72	38.5	39
Sulphate of Magnesia	.	.	1	60	32.4	32
Water	.	.	6	54	29.1	29
			—	—	—	—
			1	186	100.0	100

PHOSPHURET OF MAGNESIUM has not been examined.

HYPOPHOSPHITE OF MAGNESIA may be obtained by boiling oxalate of magnesia for a long time with hypophosphite of lime, filtering and carefully evaporating the liquid. It crystallizes in octoëdra, containing 55 per cent. of water.

PHOSPHITE OF MAGNESIA (M + p̂) requires 400 parts of water for solution, and is crystallizable. An *ammonio-phosphite of magnesia* may be formed, which is crystallizable, and difficultly soluble.

PHOSPHATE OF MAGNESIA. (M + p'.) This salt may be obtained by adding phosphoric acid to a solution of acetate of magnesia, and evaporating the mixture. According to Fourcroy, four-sided prismatic crystals of phosphate of magnesia may be obtained by mixing the aqueous solutions of phosphate of soda and sulphate of magnesia. They require about 15 parts of water at 60° for solution, and are slowly efflorescent; when heated before the blowpipe, they leave a fusible transparent glass. They are resolved by boiling water into an insoluble *subphosphate of magnesia* and a soluble *superphosphate*. The mineral called *Wagnerit* is a *sesquiphosphate of magnesia*. The crystallized *neutral phosphate* consists of

				Riffault.			
Magnesia	.	.	1	20	16.8	}	47
Phosphoric acid	.	.	1	36	30.2		
Water	.	.	7	63	53.0		
			—	—	—	—	—
			1	119	100.0	—	100

AMMONIO-PHOSPHATE OF MAGNESIA is obtained by mixing strong and warm solutions of phosphate of ammonia and phosphate of magnesia; it precipitates in the form of a white crystalline powder, or in small four-sided prisms, tasteless, and scarcely soluble in water, but readily soluble in dilute muriatic acid. Exposed to a high temperature this salt falls into powder, evolves ammonia, fuses with difficulty, and leaves an acid phosphate of magnesia. It is, according to Berzelius, a neutral double phosphate, and consists of

Ammonia . . .	1	..	17	..	11.7
Magnesia . . .	1	..	20	..	13.8
Phosphoric acid .	2	..	72	..	49.7
Water . . . .	4	..	36	..	24.8
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	1		145		100.0

When phosphate of soda is added to solution of sulphate of magnesia, previously mixed with solution of carbonate of ammonia, a salt gradually falls which has generally been considered as identical with the previous salt, but which is in fact a *subsalt*: it exists in urine, and is a common ingredient in urinary calculi. If, after having mixed a solution of magnesia and of phosphate of soda with bicarbonate of ammonia, and having put some of the solution into a watch-glass, or upon a piece of plate-glass, lines be traced upon the glass thus covered, with a glass-rod, the salt will be deposited upon the traces. This appearance, the cause of which has not been adequately explained, has been ingeniously proposed by Dr. Wollaston as a test of the presence of magnesia; a similar appearance, however, ensues in other cases of granularly-crystallized precipitates, but never where they are pulverulent.

To separate magnesia from other earths, chemists have availed themselves of the formation of this double *subphosphate*. A mixture, for instance, of lime and magnesia may be dissolved in muriatic acid; and, upon the addition of bicarbonate of ammonia, the lime is thrown down in the state of carbonate, but the magnesia is retained by the excess of carbonic acid. Filter and add a saturated solution of phosphate of soda in excess, and in a short time the *ammonio-magnesian subphosphate* falls down. In occasionally employing this process, I have never been able to throw down the whole of the magnesia, a minute portion being retained in solution, and another falling with the lime. Berzelius directs the liquid to be tested to be mixed with muriate of ammonia, then caustic ammonia added in very slight excess, and, if necessary, filtered. Oxalate of ammonia is then added, and the oxalate of lime separated by filtration. Phosphate of soda, or phosphate of ammonia with excess of base, being now dropped in, if much magnesia is present, the solution immediately becomes turbid; if very little, the precipitate is some time falling, and is accelerated by drawing lines on the glass with a glass rod, as above stated.

According to Marcet, (*Geological Trans.*, i., 236,) 11.82 grains of pure magnesia dissolved in muriatic acid, gave, by precipitation with carbonate and phosphate of ammonia, 65.8 grains of ammonio-magnesian phosphate dried at 120°. These 65.8 grs., heated to redness, left 30.8 grains of friable phosphate of magnesia, soluble in muriatic acid, and tasteless. Dr. Marcet infers that this ignited phosphate of magnesia consists of 38.5 magnesia, and 61.5 phosphoric acid *per cent.*, numbers which approximate to 1 atom of magnesia + 1 atom of phosphoric acid. (See also Henry, *Phil. Trans.*, 1810, p. 112.)

According to Berzelius (*Lehrbuch*) the ammonio-magnesian phosphate is perfectly insoluble in fluids containing phosphate of ammonia or ammonio-phosphate of soda; so that in such cases the precipitation of the magnesia is complete. It contains 38 *per cent.* of water, and loses, at a red heat, 57.44 *per cent.* of water and ammonia, and leaves 47.56 *per cent.* of neutral phosphate of magnesia. The oxygen in the water is to that in



the magnesia as 5 to 1, and the proportion of ammonia is such as to neutralize the phosphoric acid of the magnesian salt. It is probable, therefore, that the ammonio-magnesian phosphate precipitated as above, and dried at 100°, consists of

					Riffault.
Ammonia	. . .	1	. . .	17	. . . 14.41 . . . 13.880
Magnesia	. . .	1	. . .	20	. . . 16.96 . . . 16.808
Phosphoric acid	. . .	1	. . .	36	. . . 30.45 . . . 30.667
Water	. . .	5	. . .	45	. . . 33.18 . . . 38.645
		1		118	100.00 . . . 100.000

CARBONATE OF MAGNESIA. (M + car'.) This term is generally applied to the white precipitate obtained by adding carbonate of soda or potassa to a solution of sulphate of magnesia, and thoroughlyedulcorating and drying the precipitate; it is usually obtained from boiling solutions, and great attention should be paid to the purity of the water employed in washing the precipitate, and to the method of drying it. It varies somewhat in composition, and in density, when dried, according to the method adopted in its precipitation. This is the *magnesia alba* of pharmacy, and appears to be a compound of hydrate of magnesia and carbonate of magnesia, probably in the proportions of 1 atom of quadrihydrate and 1 atom of carbonate. (M + 4q) + (M + car'), or, perhaps, (M + 3q) + (M + car' + q.) It has been repeatedly analyzed, and the following are some of the results:

	Kirwan.	Bergman.	Dalton and Henry.		Klaproth.	Buchholz.		Berzelius.
			Henry.	Klaproth.	hot ppt.	cold ppt.		
Magnesia . . .	45	45	43	40	42	33		41.60 to 43.2
Carbonic acid . . .	34	25	40	33	35	32		36.58 to 36.4
Water . . .	21	30	17	27	23	35		21.82 to 20.4
	100	100	100	100	100	100		100.00 100.0

When a current of carbonic acid gas is passed through a mixture of water and magnesia, a clear solution of *bicarbonate of magnesia* is obtained, which has a bitter taste, and which, when surcharged with carbonic acid, affords a useful medicinal preparation, which is sold under the name of *magnesia water*, and is useful in some calculous affections. But a solid or crystallized bicarbonate of magnesia cannot be obtained, and the crystals which are deposited when this solution is left to spontaneous evaporation, and which are oblique rhombic prisms (Brooke, *Ann. of Phil.*, 2nd series, vi., 375), are hydrated carbonate of magnesia, composed of

					Berzelius.	Henry.
Magnesia . . .	. . .	1	. . .	20	. . . 29	. . . 29.6 . . . 30
Carbonic acid . . .	. . .	1	. . .	22	. . . 32	. . . 31.5 . . . 30
Water . . .	. . .	3	. . .	27	. . . 39	. . . 38.9 . . . 40
		1		69	100	100.0 100.

When these crystals of hydrated carbonate are put into cold water, they are decomposed, bicarbonate of magnesia is dissolved, and a subcarbonate is deposited; boiling water produces the same precipitate, but carbonic acid is evolved, and nothing remains in solution: in this case the precipitate is *magnesia alba*.

There are other processes by which the carbonate of magnesia of commerce is procured, such as by decomposing *bittern*, or impure muriate of magnesia of the sea-salt works, by magnesian limestone, or by crude carbonate of ammonia, produced by the distillation of bone; in the latter case muriate of ammonia and carbonate of magnesia result; the solution of the muriate is evaporated to dryness and sublimed with chalk; carbonate of ammonia is thus reproduced for the decomposition of a second portion of *bittern*, and so on. Carbonate of magnesia was first used in medicine early in the last century.

*Native Carbonate of Magnesia* has been found in Piedmont and Moravia, constituting the mineral called *magnesite*. It has also been found at Hoboken, in North America, in veins in a serpentine rock, accompanying the *native hydrate*. It is generally white and friable, and in some places in fine acicular crystals. A variety of *native carbonate of magnesia*, brought from the East Indies by Mr. Babington, has been described and analyzed by Dr. Henry (*Ann. of Phil.*, i., 254). It is white, massive, hard, of a conchoidal fracture, and translucent at the edges; specific gravity 2.6. It slowly dissolves in acids, and is composed of 1 atom of magnesia + 1 atom carbonic acid.

AMMONIO-CARBONATE OF MAGNESIA is obtained by mixing excess of bicarbonate of ammonia with muriate of magnesia; it forms very small crystals, which are gradually deposited, and which are decomposed by hot water, and by exposure to air.

CARBONATE OF POTASSA AND MAGNESIA. When excess of bicarbonate of potassa is mixed with muriate of magnesia, no precipitation ensues, but in a few days crystals are formed, of an alkaline taste, which are decomposed by hot water. They may be regarded as a hydrated compound of 1 atom of bicarbonate of potassa + 2 atoms of carbonate of magnesia, for they consist of

Potassa	.	.	1	..	48	..	18.4	..	Berzelius.
Magnesia	.	.	2	..	40	..	15.6	..	18.28
Carbonic Acid	.	.	4	..	88	..	34.4	..	15.99
Water	.	.	9	..	81	..	31.6	..	34.49
			—		—		—		31.24
			1		257		100.0		100.00

CARBONATE OF SODA AND MAGNESIA is formed as the triple potassa-salt, by bicarbonate of soda; but it is not so easily decomposed; and, accordingly, when magnesia is precipitated by excess of carbonate of soda, a portion of the triple soda-salt is retained, and not easily washed away.

CARBONATE OF LIME AND MAGNESIA is the mineral known under the name of *bitter-spar*; it has the primitive form of carbonate of lime, and consists of 1 atom of each of its component carbonates.

BORATE OF MAGNESIA may be formed artificially, by boiling boracic acid and magnesia in water; as the solution cools, it deposits the salt in crystalline grains. Paper which has been moistened with it burns with a fine green flame; at a red-heat it runs into a transparent glass. It occurs native in a mineral called *boracite*, hitherto only found in the duchy of Luneburgh. Its primitive form is the cube, but the edges and angles are generally replaced by secondary planes, and four of the angles are always observed to present a greater number of facets than the other

four: these crystals become electric by heat; the most complex angles being rendered positive, and the simplest negative. It sometimes contains lime. It appears to consist of

						Arfwedson.	Stromeyer.					
Magnesia	.	.	$1\frac{1}{2}$	..	30	..	30.62	..	30.3	..	33	
Boracic Acid	.	.	1	..	63	..	69.38	..	69.7	..	67	
		—			—			—			—	
		1	98			100.00			100.0			100.

THE SALTS OF MAGNESIA are, for the greater part, soluble in water, and afford precipitates of magnesia, and of carbonate of magnesia, upon the addition of pure soda, and of carbonate of soda. Phosphate of soda occasions no immediate precipitate when added to a magnesian salt, but the subsequent addition of ammonia causes a white precipitate of the triple ammonio-magnesian phosphate. The pure magnesian salts, when heated before the blowpipe with a little nitrate of cobalt, furnish pale rose-coloured compounds.

MAGNESIAN MINERALS are generally soft and apparently unctuous to the touch; they have seldom either lustre or transparency, and are generally more or less of a green colour. *Steatite* or *soapstone*, *talc*, and *asbestos*, may be taken as instances. The *chrysolite* also contains more than half its weight of magnesia. The mineral called *bitter-spar*, of which the finest specimens come from the Tyrol, contains 45 per cent. carbonate of magnesia, 52 carbonate of lime, and a little iron and manganese. Its primitive crystal is a rhomboid nearly allied to that of carbonate of lime; its angles being  $106^{\circ} 20'$ , and  $73^{\circ} 80'$ . It is of a yellowish colour, and a pearly lustre; semi-transparent and brittle. A variety found at *Miemo* in Tuscany, has been called *Miemite*. The species of marble, termed *Dolomite*, found in the Alps, at *Icolmkill* in Scotland, and elsewhere, contains also a large quantity, generally 40 per cent. of carbonate of magnesia. The same may be said of the *magnesian limestone* of Derby and Nottingham: it is generally of a yellowish colour, and less rapidly soluble in dilute muriatic acid, than the purer limestone, whence the French have termed it *chaux carbonatée lente*. The lime which it affords is much esteemed for cements, but for agricultural purposes it is often mischievous, in consequence of its remaining caustic for a very long time, and thus injuring the young plant.

The separation of magnesia and lime is a problem of some importance in analytical chemistry, as they often exist together in the same mineral, more especially in the varieties of magnesian limestone. When solution of carbonate of ammonia is added to the mixed solution of lime and magnesia in nitric or muriatic acids, carbonate of lime falls, and the magnesia is retained in solution, and may be separated by boiling with carbonate of potassa: this method, however simple, is not susceptible of great accuracy, for a portion of carbonate of lime will always be retained along with the magnesia in solution, and a triple ammoniaco-magnesian salt is also formed. Mr. R. Phillips (*Quarterly Jour.*, vi., 317) proposes the following process: "To the muriatic or nitric solution of lime and magnesia, add sulphate of ammonia in sufficient quantity; evaporate the mixture gradually to dryness, and then heat to redness till it ceases to lose weight, by the volatilization of the muriate or nitrate of ammonia formed: note the weight of the mixed salt, reduce it to powder, and wash

it with a saturated solution of sulphate of lime till all the sulphate of magnesia appears to be dissolved; dry the sulphate of lime left, and by deducting its weight from that of the mixed sulphates, the quantity of sulphate of magnesia dissolved will appear." After repeated trials of the various modes of separating lime and magnesia, I am induced to consider the following as tolerably correct. To the mixed solution of lime and magnesia add oxalate of ammonia slightly acid, collect the precipitate, wash, and dry it at  $212^{\circ}$ : 100 parts indicate between 38 and 39 of lime. If nitric acid were used for solution, the magnesia may afterwards be obtained by evaporation and heating the residue to redness in a platinum crucible till it ceases to lose weight. If sulphuric acid were the solvent, the same operation affords dry sulphate of magnesia, of which 60 parts are equivalent to 20 magnesia; or the magnesia may, in other cases, be precipitated by phosphate of ammonia as above stated, (p. 626.) In the analysis of minerals which contain magnesia, and which resist the action of acids, fusion with alkaline bodies must be resorted to. As instances of these analyses the reader is referred to Klaproth's examination of the *chrysolite*, and of *olivine*, in the 7th and 8th sections of the first volume of his *Analytical Essays*. See, also, Rose's *Analytical Chemistry*.

### § VIII. MANGANESE.

THE common ore of manganese is the black, or *peroxide*, which is found in considerable abundance, and is of important use in the arts: this metal also occurs in a few animal products, and is not uncommonly discovered in the ashes of vegetables. Particular attention was first directed to the black oxide of manganese by Scheele, in 1774, and shortly afterwards Gahn found that it contained a peculiar metal, which he first called *magnesium*, but which was afterwards termed *Manganese*.

In some respects it resembles the metals already described; in others, it is eminently different. Like them, it has a powerful affinity for oxygen, speedily attracting it from air and water; and its oxides are extremely difficult of decomposition: they have, however, nothing in common with alkaline bodies; and manganese, in its highest state of oxidizement, constitutes an acid.

To obtain metallic manganese, the *carbonate of manganese* may be mixed into a paste with oil, and subjected to heat gradually raised to redness, in a glass or earthen retort, or other close vessel. The carbonaceous mixture thus obtained is then rammed into a good crucible, which is filled up with charcoal-powder, and subjected for two hours to the strong white-heat of a wind-furnace: a metallic button is thus obtained, which is manganese, containing a little carbon and silicium, from which it may be freed, according to Dr. John, by fusion with borax in a crucible coated with charcoal: it is doubtful, however, as Berzelius has observed, whether in this case it does not contain a little boron.

When the *tartrate of manganese and potassa* is intensely heated in a wind-furnace, it furnishes globules of metallic manganese; and as this salt is easily obtained in a state of purity, its decomposition is perhaps

the simplest process for obtaining the pure metal, care being taken to exclude foreign substances derivable from the fuel or from the crucible.

Manganese is a hard gray metal, exhaling a peculiar odour when handled or breathed upon; it is brittle, and has a granular and sometimes a slightly crystalline fracture; its specific gravity is 8.013 according to John, but 6.8 according to Bergmann. When pure, it does not affect the magnetic-needle, but often does so from containing a trace of iron. It is softer than cast-iron, and admits of filing, yet brittle enough to be reduced into an iron-gray metallic powder. It is best preserved in naphtha; for in the air it soon tarnishes and crumbles down into a black powder, and undergoes the same change in water, with the evolution of hydrogen gas. It may also be conveniently kept in a small glass tube hermetically sealed. The equivalent of manganese may be assumed as = 28. (28.5 Gmelin. 27.7 Turner.)

**MANGANESE AND OXYGEN.** There are four compounds of manganese and oxygen, three of which are oxides, and one an acid.

**PROTOXIDE OF MANGANESE** (*man* + *O*) or **MAN**, is obtained (1), by passing a current of hydrogen over the pure deutoxide or peroxide of manganese, contained in a porcelain or iron tube, exposed to a heat gradually raised to bright redness: water is formed, and a dingy-green powder remains in the tube, which is the *protoxide*. (2.) It may also be procured by mixing the peroxide with half its weight of muriate of ammonia, and projecting the mixture in successive portions into a red-hot crucible; the product is lixivated, and the solution of chloride of manganese\*, thus obtained, is decomposed by the addition of carbonate of potassa; the precipitate is collected, washed, dried, and exposed, out of the contact of air, to an intense heat; or it may be heated in a tube, through which a current of hydrogen is passed. (3). Wöhler and Liebig obtain it by fusing chloride of manganese with twice its weight of carbonate of soda; the resulting chloride of sodium is removed by washing from the residuary protoxide of manganese.

**HYDRATED PROTOXIDE OF MANGANESE.** When the solution of chloride of manganese is decomposed by a solution of potassa, a bulky white precipitate falls, which is a *hydrated protoxide* of manganese, containing, according to Davy, 24 per cent. of water; it very speedily becomes brown by exposure to air, in consequence of the absorption of oxygen, and, when collected and washed upon a filter, it becomes a brown powder, which is a hydrate of the deutoxide.

The protoxide of manganese is not altered, when dry, by exposure to air: When heated, it absorbs oxygen, and is converted into deutoxide; and at a temperature of about 600° is said, by Forchammer and Arfwedson, to take fire. It is readily soluble in the dilute acids, and is the basis of all the ordinary manganesian salts. When put into concentrated sulphuric acid, it evolves intense heat. Its solutions and salts are nearly colourless when perfectly pure, but they generally acquire a slightly-pink hue, probably from the presence of a minute quantity of manganic acid. When ammonia is added to the solutions of this oxide, the whole

\* In this process, so long as there is excess of the oxide, the manganese only is converted into chloride, and other metals that may be present are not rendered soluble.

is not precipitated, but it forms a triple salt, as is the case with magnesia\*. The equivalent number of manganese deduced from the composition of this oxide is 28, and the oxide consists of

					Forchhammer.	Berzelius and Arfwedson.	Davy.
Manganese	1	..	28	..	77.75	..	79
Oxygen	1	..	8	..	22.25	..	21
	<u>1</u>		<u>36</u>		<u>100.00</u>		<u>100</u>

SESQUIOXIDE OF MANGANESE; DEUTOXIDE OF MANGANESE. (*man* +  $1\frac{1}{2}O$ .) When protoxide, or carbonate of manganese, is exposed for some time to a red-heat in an open vessel, it absorbs oxygen, and is converted into a deep-brown powder. An oxide similarly constituted is also obtained by heating the pure peroxide of manganese till it ceases to give out oxygen, in a platinum crucible. When ammonia is added to the pink solution obtained by triturating a mixture of peroxide of manganese and binoxalate of potassa with water, a precipitate is obtained, which, when well washed and heated red-hot, is similar in composition to the above. The characters of this oxide, in respect to solvents, differ with its state of aggregation; but it does not form permanent or definite salts; for such of its acid solutions which are at first red, become colourless when heated, or when exposed to air and light, and deposit peroxide, while a portion of protoxide remains in solution. This oxide consists of

					Forchhammer.	Arfwedson and Berzelius.	
Manganese	1	..	28	..	70	..	72.74
Oxygen	$1\frac{1}{2}$	..	12	..	30	..	27.26
	<u>1</u>		<u>40</u>		<u>100</u>		<u>100.00</u>

Or it may be considered as consisting of one proportional of the protoxide, combined with one of the peroxide.

HYDRATED SESQUIOXIDE OF MANGANESE is obtained by exposing the moist protoxide to the action of air, and contains about 10 per cent. of water. It is a common natural product, occurring crystallized and massive, and so closely resembling the peroxide, that it is often difficult to distinguish them; the powder of the hydrated deutoxide is, however, generally *brown*, that of the peroxide *black*; the former, heated in a tube, gives off water and little oxygen; the latter, little moisture, and much oxygen. Heated by the blowpipe with glass of borax, the sesquioxide of manganese dissolves with a red or violet colour in the outer flame; in the inner flame it becomes colourless in consequence of deoxidization, but reacquires colour when transferred to the outer oxidizing flame.

PEROXIDE OF MANGANESE. (*man* +  $2O$ .) This is the oxide which most commonly occurs *native*, and is resorted to as the source of the other combinations of this metal. In this country it is common in Devonshire, Somersetshire, and Aberdeenshire. It is found in a variety

\* If manganesic solutions contain silica, (as is often the case, and especially in the analysis of ores and minerals containing manganese,) the silica falls in combination with the oxide of manganese, when they are precipitated by an alkali; it may be separated by dissolving the moist precipitate in muriatic acid, evaporation to dryness, and washing. (Berzelius.)

of forms: compact and massive, pulverulent and crystallized. Many of the latter varieties have a gray metallic lustre, and are found acicularly radiated, and in rhomboidal prisms. It also occurs with the native sesquioxide, forming the *oxidum manganoso manganicum* of Arfwedson, and the *Varvicite* of Phillips, but the exact composition of these native oxides can scarcely be determined by their external characters. Under the name of *manganese*, this substance is met with in commerce, and is largely consumed in the manufacture of bleaching-compounds. In the laboratory, it is resorted to as a source of oxygen gas, but it sometimes is fraudulently mixed with carbonaceous matter, and then yields carbonic acid. It also generally gives off a little nitrogen upon the first application of heat, the source of which is not obvious. Carbonate of lime, sulphate of baryta, oxide of iron, and several other substances, are frequently associated with it. It is also used to give a black colour to earthenware, to remove the brown colour which glass derives from peroxide of iron, and is sometimes employed to sweeten foul water at sea, or to prevent its becoming so. It usually loses considerably in weight, on being dried at a temperature not exceeding  $300^{\circ}$ ; at a red-heat it becomes *sesquioxide*, and, intensely heated in an iron tube, or with a minute quantity of carbonaceous matter, part of it becomes *protoxide*. It is not altered by air or water. It forms no combinations with the acids; but such of them as appear to dissolve it, reduce it to the state of protoxide. Gently heated with muriatic acid, chlorine is liberated, in consequence of the decomposition of the acid by the oxygen of the oxide, which is reduced to the state of protoxide, and thus dissolved. Boiled with sulphuric acid, oxygen is evolved, and a soluble *sulphate of the protoxide* is formed, together with a small portion of *manganic acid*, which gives the solution a pink colour and bleaching properties. Nitric acid does not attack it unless it contains sesquioxide, or some deoxidizing agent be at the same time present.

A solution of the protoxide free from iron may be obtained from the common peroxide by digesting it in muriatic acid as long as chlorine escapes; filter the solution, and drop into it a solution of ammonia till the acid is saturated, and the alkali remains in slight excess; if oxide of iron is present, it is thus precipitated; excess of ammonia throws down protoxide of manganese; or it may be more perfectly precipitated by potassa. A chloride of manganese, prepared, as above directed, by heating excess of the peroxide with muriate of ammonia, is also a source of the pure protoxide. Peroxide of manganese consists of

					Forchammer.	Berzelius and Arfwedson.			
Manganese . . .	1	. . .	28	. . .	63.5	. . .	63.75	. . .	64.02
Oxygen . . . . .	2	. . .	16	. . .	36.5	. . .	36.35	. . .	35.98
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		44		100.0		100.00		100.00

HYDRATED PEROXIDE OF MANGANESE is obtained, according to Berthier, by passing chlorine through the protocarbonate of manganese diffused in water; a black powder falls, which, when washed and carefully dried, consists of 88 peroxide and 12 water\*. A hydrated peroxide (con-

\* Peroxide of manganese exhibits | ters; it is a conductor of electricity, and  
some singular electrochemical charac- | becomes highly electro-negative in con-

sisting of 1 atom of peroxide and 1 of water,) is formed by precipitating protochloride of manganese by chloride of lime. The soft black mineral known to our miners under the name *Wad*, is also a hydrate of the peroxide of manganese: it contains 2 atoms of water.

Pure peroxide of manganese is sometimes useful as a test of the presence of iodine, bromine, and chlorine. When mixed with a salt containing iodine, and the mixture heated with a little sulphuric acid, the violet vapour of iodine is evolved; the salts of bromine give in the same way a brown vapour; and from the muriatic salts chlorine is evolved.

**MANGANESIC ACID; MANGANIC ACID.** When peroxide of manganese is heated to redness with nitrate of potassa, a compound is obtained, which, when put into water, furnishes a solution exhibiting various tints of green, purple, and red, and which was therefore called *Chameleon Mineral*. A similar compound is more perfectly obtained by fusing the peroxide with caustic potassa, which furnishes a green substance when the alkali is in excess, but black if the oxide predominate; the former gives a green, the latter a pink solution, both of which, when duly diluted, exhibit various changes of tint, and ultimately become colourless, with the deposition of a brown powder. It was ascertained by Chevillot and Edwards, in 1818, that this compound could not be obtained in close vessels, but that, air being present, oxygen was absorbed. On evaporating the pink solution, they obtained crystals, which they found to be a true salt of potassa with manganic acid\*. This salt, when acted upon by concentrated sulphuric acid, evolves a purple vapour, which condenses in red streaks, and presently decomposes and deposits peroxide. Frommherz succeeded in obtaining manganic acid as follows:—Two parts of nitrate of baryta are mixed with one of peroxide of manganese, and exposed to a red-heat: a green mass is obtained, which is to be reduced to fine powder, mixed with 25 parts of water, and a stream of carbonic acid passed through the mixture, which is kept constantly stirred; carbonate of baryta is formed, and a deep violet-coloured solution of manganic acid. When the diffused powder has lost its green colour, the fluid is poured clear off, and boiled for a quarter of an hour to expel excess of carbonic acid, during which a portion of carbonate of baryta and of peroxide of manganese are precipitated: the clear fluid is boiled down to one-fourth its bulk, again left to become clear, and ultimately evaporated to a small bulk: during this evaporation, oxide of manganese is again separated, in consequence of the decomposition of a part of the acid; but the residuary solution forms acicular crystals of *hydrated manganic acid*, on cooling (containing 8.5 per cent. of water). All attempts have failed to deprive this acid of water. Its solution has a peculiar astringent taste, possesses considerable bleaching powers, (hence *chlorine* has often been erroneously suspected in these solutions,) and exhibits a violet-colour by transmitted light, but appears of a carmine-red by reflected light: it tinges

tact with other metals, whilst metallic manganese is under such circumstances eminently electro-positive: the peroxides in general probably possess similar electrical relations.

\* The pink solution of manganate of potassa is immediately rendered yellow

by a very minute addition of white arsenic, so that it has been proposed as a test of that poison; but it can only be depended on in conjunction with others, as it is discoloured, though not so readily, by other deoxidizing substances.



the skin brown. It is decomposed by boiling, especially when diluted; and also by exposure to the sun's rays.

Chlorine has no effect on manganic acid, but iodine decomposes it, and becomes iodic acid. It is decomposed by hydrogen, sulphur, and phosphorus, by the hydracids, and by carburetted hydrogen and carburet of sulphur, and all organic substances; hence it cannot be filtered, being decomposed by the paper; it oxidizes the metals. With potassa, soda, baryta, and strontia, it forms definite salts, but apparently not with other salifiable bases.

The exact composition of this acid has scarcely been determined, but it probably consists of

				Unverdorben.	Frommherz.				
Manganese . .	1	..	28	..	58.2	..	58.74	..	59.45
Oxygen . . .	2½	..	20	..	41.8	..	41.26	..	40.55
	<u>1</u>		<u>48</u>		<u>100.0</u>		<u>100.00</u>		<u>100.00</u>

PERMANGANIC ACID. It is supposed by Mitscherlich, that the salt obtained by adding peroxide of manganese to fused chlorate of potassa, (Wöhler, *Poggendorff*, xxvii., 626,) contains manganese in the highest state of oxidizement, that is, combined with 3.5 atoms of oxygen, but the exact composition of the green, pink, and purple salts cannot be considered as satisfactorily ascertained. The peculiar green tint obtained by heating compounds of manganese with potassa, is usefully resorted to as a ready means of recognising that metal before the blowpipe. It has often been stated that pink solutions, obtained by certain acids from the peroxide, contain the sesquioxide; but some experiments, in reference to this subject, made by Mr. Pearsall, in the laboratory of the Royal Institution, render it probable that the appearance of a pink colour is always indicative of the presence of manganic acid. (*Royal Instit. Journ.*, Aug., 1831, p. 49.)

MANGANESE AND CHLORINE; PROTOCHLORIDE OF MANGANESE (*man* + *C*). Metallic manganese burns in chlorine. When peroxide of manganese is heated with muriate of ammonia, as above directed (page 631), a solution of *chloride of manganese* is easily obtained from the residue, which, if evaporated by a gentle heat, furnishes transparent pinkish crystals, soluble in water and alcohol. The same salt is obtained by dissolving carbonate of manganese in dilute muriatic acid. Exposed, out of the contact of air, to a heat gradually raised to redness, this substance loses water, to the amount of about 40 per cent., and forms a lamellar *anhydrous chloride of manganese*. Heated in the contact of air, this chloride is decomposed and converted into an oxide: it consists of

				J. Davy.	Arfwedson.				
Manganese . .	1	..	28	..	43.7	..	46	..	44.25
Chlorine . . .	1	..	36	..	56.3	..	54	..	55.75
	<u>1</u>		<u>64</u>		<u>100.0</u>		<u>100</u>		<u>100.00</u>

PERCHLORIDE OF MANGANESE has been described by M. Dumas, formed by adding fused chloride of sodium to a sulphuric solution of manganic acid; the compound passes off in the form of a green vapour, condensable at 0° into an olive-coloured liquid. If the vapour be conveyed into a moistened flask it acquires a red tint, and muriatic and manganic acids

are generated. The simplest process for preparing it consists in forming a green chameleon-mineral by fusing peroxide of manganese with potassa, and pouring dilute sulphuric acid upon it, by which a manganesiate and sulphate of potassa are obtained. By the affusion of strong sulphuric acid these salts yield a solution of manganesic acid, to which small pieces of fused common salt are added, as long as green vapour is evolved. (*Edin. Journ. of Science*, viii., 179.) From the phenomena of its decomposition, this chloride is supposed to consist of 1 atom of manganese and  $2\frac{1}{2}$  of chlorine.

AMMONIO-MURIATE OF MANGANESE is a soluble and crystallizable salt, not decomposed by excess of ammonia.

CHLORATE OF MANGANESE has not been examined.

IODIDE OF MANGANESE is a soluble colourless compound. The *iodate* has not been examined.

FLUORIDE OF MANGANESE is formed, according to Dumas and Wöhler, by mixing the green chameleon-mineral with half its weight of pure fluor-spar in fine powder, and decomposing the mixture in a platinum vessel by anhydrous sulphuric acid: a vapour, of a deeper tint than chlorine, is evolved, which acquires a red colour on mixture with atmospheric air, and gives a red solution in water of hydrofluoric and manganesic acids. It is decomposed by the contact of glass, fluosilicic acid is formed, and a brown powder deposited, which appears to be anhydrous manganesic acid. This fluoride probably consists of one proportional of manganese and two and a half proportionals of fluorine. When carbonate of manganese is digested in hydrofluoric acid, amethyst-coloured crystals may be obtained by evaporation, probably of *hydrated protofluoride of manganese*.

NITRATE OF MANGANESE. ( $MAN + N'$ .) Dilute nitric acid readily dissolves protoxide of manganese, and forms a very soluble, deliquescent and difficultly-crystallizable *protonitrate*. The same salt may be obtained by digesting peroxide of manganese in nitric acid with a portion of gum or sugar, which abstracts oxygen, carbonic acid is evolved, and the protoxide dissolved by the acid. Exposed to light, the solution of the protonitrate lets fall a portion of peroxide of manganese. When dilute nitric acid is poured upon the deutoxide of manganese, a protonitrate and peroxide are formed.

The crystallized protonitrate of manganese consists, according to Thomson, of

Protoxide of manganese	.	1	..	36	..	23.5
Nitric acid	.	1	..	54	..	35.4
Water	.	7	..	63	..	41.1
		<hr/>		<hr/>		<hr/>
		1		153		100.0

SULPHURET OF MANGANESE. ( $man + S$ .) When dried protosulphate of manganese is ignited with one-sixth its weight of finely-powdered charcoal, or when a current of sulphuretted hydrogen is passed over the protosulphate heated to redness, a true *sulphuret of manganese* is obtained. (Berthier, *Ann. de Chim. et Phys.*, xxiv., 273; Arfwedson, *Ann. of Phil.*, vii., 332.) It has a gray metallic lustre. It is perfectly soluble in dilute sulphuric and muriatic acid, with the evolution of sulphuretted hydrogen

gas. It is identical with the *native* sulphuret of manganese, a rare ore, found in Cornwall and Transylvania. It consists of

				Dobereiner.		Arfwedson.	
						<i>Artificial.</i>	<i>Native.</i>
Manganese	. 1 . 28 . 63.6	. 65.86	. 63.13	. 62.58			
Sulphur	. . 1 . 16 . 36.4	. 34.14	. 36.87	. 37.42			
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1 44 100.0	100.00	100.00	100.00	100.00	100.00	

When sulphur is heated with peroxide of manganese, sulphurous acid is evolved, and a greenish substance obtained, which also appears to be a compound of manganese and sulphur, and not, as has often been supposed, a sulphuretted oxide. A reddish-brown *hydrosulphuretted oxide of manganese* is thrown down from solutions of the protoxide by the alkaline hydrosulphurets. When heated, it evolves water, and becomes a sulphuret of manganese.

When a solution of protosulphate of manganese is mixed with a solution of carburet of sulphur in caustic potassa, a gray-precipitate falls, which, when stirred so as to bring it to the surface, assumes a fine purple colour: this gradually disappears, and the precipitate assumes the red or orange colour of sulphurets of manganese. (Berzelius.)

HYPOSULPHITE OF MANGANESE ( $\text{MAN} + \underline{\text{S}}$ ) remains in solution when sulphate of manganese is decomposed by hyposulphite of lime. It has not been further examined.

SULPHITE OF MANGANESE ( $\text{MAN} + \underline{\text{S}}$ ) is obtained by passing sulphurous acid through a mixture of carbonate of manganese and water till the carbonic acid is expelled. It is a white granular tasteless powder, insoluble in water and in alcohol, and not altered by exposure to air. It dissolves in excess of sulphurous acid, and is decomposed by heat. (Berzelius.)

HYPOSULPHATE OF MANGANESE. ( $\text{MAN} + \underline{\text{S}'}$ .) When peroxide of manganese (previously digested in nitric acid, and thoroughly washed to deprive it of hydrated oxide) is diffused through water, and sulphurous acid passed into it, a neutral hyposulphate of the protoxide is obtained. It affords a deliquescent salt on evaporation. (See p. 431.)

SULPHATE OF MANGANESE ( $\text{MAN} + \text{S}'$ ) is formed by dissolving the protoxide or protocarbonate in dilute sulphuric acid, and evaporating: a *protosulphate* is formed, which crystallizes in rhomboidal prisms, slightly efflorescent in a dry atmosphere, soluble in 2.5 of water, and of a bitter styptic taste. When heated it crumbles down into a white *anhydrous sulphate*, and this, at a bright red-heat gives out oxygen, sulphurous acid, and some anhydrous sulphuric acid, and a deutoxide of manganese remains. Sulphate of manganese may also be obtained by mixing peroxide of manganese into a paste with sulphuric acid, and heating it in a basin nearly to redness: oxygen is evolved, and the dry mass washed with water affords the sulphate. The crystals of this salt have generally more or less of a pink hue, from a trace of manganic acid.

Sulphate of manganese with excess of sulphuric acid forms an uncrystallizable supersulphate. When chlorine is passed through a solution of the neutral sulphate it is decomposed, peroxide is precipitated, supersulphate formed, and muriatic acid is found in the solution. The crystallized protosulphate of manganese consists of

						John.	Mitscherlich.
Protoxide of Manganese	1	..	36	..	32.2	..	31.00
Sulphuric Acid	.	1	..	40	..	35.6	..
Water	.	.	4	..	36	..	35.34
			<hr/>		<hr/>		<hr/>
	1		112		100.0		100.00
							68
							32
							100.

AMMONIO-SULPHATE OF MANGANESE is a soluble and crystallizable salt, obtained when sulphate of ammonia and sulphate of manganese are mixed in atomic proportions. Its crystals contain eight proportionals of water, and are of a pale rose-colour.

POTASSA-SULPHATE OF MANGANESE forms colourless crystals, containing six proportionals of water.

PHOSPHURET OF MANGANESE (*man + p*) is of a blue-white metallic lustre, and considerably inflammable: it is permanent in the air, brittle, and easily fused.

PHOSPHITE and HYPOPHOSPHITE OF MANGANESE have not been examined.

PHOSPHATE OF MANGANESE (*MAN + p'*) is precipitated in the form of a white nearly insoluble powder, by adding phosphate of soda to sulphate of manganese. Berzelius observes, that in analyses, this salt is difficultly distinguished from phosphate of lime and phosphate of magnesia. It is, however, decomposed by boiling with caustic potassa, and the oxide assumes a dark colour.

CARBURET OF MANGANESE. (*man + car.*) When the metal reduced from its oxide is heated with charcoal, it often assumes a lamellated appearance, from combining with that element. Carburet of manganese is also not uncommonly met with in combination with carburet of iron in some varieties of cast iron.

CARBONATE OF MANGANESE (*MAN + car'*) is white, or pale-red, insipid, and insoluble in water. It is precipitated as a hydrate, by alkaline carbonates, from the protochloride or protosulphate. When heated it loses water and becomes brown. It is found *native*, constituting the *spathose ore of manganese*, which is anhydrous. When the artificial carbonate is carefully dried at 100° it probably consists of

						Forchammer.
Protoxide of Manganese	1	..	36	..	53.55	..
Carbonic Acid	.	1	..	22	..	32.80
Water	.	.	1	..	9	..
			<hr/>		<hr/>	
	1		67		100.00	
						100.000

CYANURET OF MANGANESE falls in the form of a gray insoluble precipitate, when solution of cyanuret of potassium is added to a protosalt of manganese. The precipitate is soluble in excess of the precipitant, and the solution yields, on evaporation, brown acicular crystals.

SULPHOCYANURET OF MANGANESE is a colourless soluble salt.

BORATE OF MANGANESE (*MAN + bor'*) is precipitated in the form of a white powder when solution of borate of soda is mixed with protosulphate of manganese. If the salt of manganese be mixed with a salt of magnesia, borax occasions no precipitate, and the borate is itself soluble in sulphate of magnesia. (Berzelius.)

CHARACTERS OF THE SALTS OF MANGANESE. The salts of manganese, containing the protoxide, are mostly soluble in water: the solution is

colourless or slightly pink, of a bitterish astringent taste, and often becomes turbid and brown by exposure to air. They are not precipitated by hydriodic acid, nor by tincture of galls; they furnish white precipitates with the alkalis, which soon become discoloured by exposure to air. The alkaline carbonates throw down white precipitates, which gradually assume a hue of purple; they are precipitated white by ferrocyanuret of potassium, and orange or reddish-brown by hydrosulphuret of ammonia. Ammonia only throws down half the oxide, and forms a triple salt with the remainder; or, if there be excess of acid, the triple salt only is formed, and there is no precipitation. Manganese is not thrown down in the metallic state by any of the other metals. The sulphate and the muriate are used in calico-printing.

Before the blowpipe *oxide of manganese* gives, with microcosmic salt in the exterior flame, a fine amethyst colour, which disappears in the interior flame. With borax it gives a yellowish or reddish glass. When the manganese, from its combination with iron, or any other cause, does not produce a sufficiently intense colour in the glass, a little nitre may be added to it while in a state of fusion, and the glass then becomes dark-violet while hot, and reddish-violet when cool. It is not reduced.

### § IX. IRON.

THE most important native combinations of iron, whence the immense supplies for the arts of life are drawn, are the *oxides*: it is also found combined with sulphur, and with several acids; it is so abundant that there are few fossils free from it. It is found in small quantity in some animal and vegetable bodies; and in several mineral waters. The alchemists distinguished it by the name and symbol of Mars ♂.

Iron is a metal of a blue-white colour, fusible at a white heat. Its sp. gr. is 7.77. It probably has not been so long known as some of the other metals; it was, however, employed in the time of Moses for cutting-instruments. It is extremely ductile, but cannot be hammered out into very thin leaves. It is very tenacious; and at a bright red-heat is extremely pliable, and admits of being *welded* or joined by hammering to another piece of the red-hot metal. It is attracted by the magnet, but does not retain magnetism when perfectly pure; and at a bright red-heat becomes perfectly indifferent to it. It is combustible at a very high temperature, as is beautifully seen in the experiment of burning it in oxygen gas, or sprinkling its filings into the flame of a spirit-lamp.

*Native Iron.* Iron is sometimes found *native*, and is usually regarded as of meteoric origin, for it is invariably alloyed by a portion of the metal nickel, and a similar alloy is found in *meteoric stones*. It is flexible, cellular, and often contains a green substance of a vitreous appearance. It has been found in Africa, in America, and in Siberia, where a mass of it, weighing 1600 lbs., was discovered by Professor Pallas. The mass found in Peru, described by Don Rubin de Celis, weighed 15 tons. In the year 1751, a mass of the same substance was seen to fall from the atmosphere in Croatia. It appeared as a large globe of fire, and is preserved in the imperial museum of Vienna. (See *Nickel*.)

IRON AND OXYGEN. Exposed to heat and air, iron quickly oxidizes and becomes converted into protoxide or peroxide, according to circum-

stances. It is only susceptible of two definite degrees of oxidizement, and both its oxides are salifiable bases.

PROTOXIDE OF IRON. ( $fe + o$ ) or Fe. (1.) When a solution of protosulphate of iron is precipitated by potassa, and the precipitate washed out of the contact of air, and dried at a red-heat, it is black, and nearly pure *protoxide*. In drying, however, oxygen is always absorbed, and a small portion of peroxide is formed. When thus recently precipitated and moist, it is sparingly soluble in ammonia, and in carbonated alkalis. (2.) Protoxide of iron may also be obtained by burning iron in oxygen gas: this very beautiful experiment was devised by Dr. Ingenhousz, and is best performed by attaching a straight piece of watch-spring, wound round with harpsichord-wire, to the stopper of an air-jar of oxygen gas; the end of a brimstone match may be attached to the wire, and inflamed at the time of plunging it into the gas; it heats the wire red-hot, which then burns and drops in black globules of oxide into the water beneath. A splendid combustion of iron is also effected by placing a small cast-iron nail upon a piece of ignited charcoal under a stream of oxygen gas issuing from a blowpipe. (3.) A similar oxide of iron used to be prepared for pharmaceutical use, by moistening iron-filings with a small quantity of water, and exposing them to the air for a day or two; a quantity of black oxide forms, which is separated by washing, and the process repeated till the whole of the metal is thus oxidized. It was called *martial ethiops*. It is black, tasteless, and insoluble in water; but it contains a portion of peroxide. (4.) Perhaps the least exceptionable process for obtaining protoxide of iron, consists in passing steam over pure iron-wire heated to redness in a porcelain tube. It is dark gray, or nearly black, brittle, and often has some lustre; and after it has been ignited, it is difficultly soluble in the acids; they do, however, dissolve it, and form solutions precisely analogous to those procured by employing metallic iron. (5.) When hydrogen gas is passed over peroxide of iron, heated to redness in a porcelain tube, water is formed, and a black powder is obtained which, according to some, is metallic iron, according to others, a suboxide. It is often pyrophoric, and is probably a mixture of metallic iron and protoxide.

It is, however, very difficult, if not impossible, to obtain a perfectly pure protoxide of iron in an insulated state, but its composition may be satisfactorily inferred by the quantity of hydrogen gas which is evolved during the action of diluted sulphuric acid upon pure iron; the equivalent of iron, thus deduced, is 28 (27, Gmelin; 27.16, Berzelius; 27.8, Stromeyer; 28.3 Gay Lussac; 28, Turner), and the protoxide consists of

					Dobereiner.	Buchholz.	Berzelius.	Gay Lussac.						
Iron	. . .	1	. . .	28	. . .	77.8	. . .	76.9	. . .	77	. . .	77.62	. . .	77.94
Oxygen	. . .	1	. . .	8	. . .	22.2	. . .	23.1	. . .	23	. . .	22.38	. . .	22.06
		<u>1</u>		<u>36</u>		<u>100.0</u>		<u>100.0</u>		<u>100</u>		<u>100.00</u>		<u>100.00</u>

HYDRATED PROTOXIDE OF IRON. When the protosalts of iron are decomposed by caustic potassa a precipitate falls, which, at the first moment, is white, but which immediately becomes gray, then green and blue, and lastly yellow, in consequence of absorbing oxygen. The white precipitate is probably an *hydrated protoxide of iron*: when boiled with

water it becomes black, the hydrate not being a permanent compound at a boiling heat.

**PEROXIDE OF IRON.** ( $fe + 1\frac{1}{2}O.$ ) When protoxide of iron is boiled in nitric acid, and precipitated by ammonia, washed, and dried at a low red-heat, it increases in weight, and acquires a brown colour. When a solution of iron in nitromuriatic acid is precipitated by an alkali, a bulky brown *hydrated peroxide of iron* falls, which, when dried, assumes a deeper colour, and is *anhydrous peroxide*. When sulphate of iron is decomposed by a very high temperature, a red powder remains, which is also the peroxide, and which was formerly called *colcothar*. It is also formed by deflagrating iron-filings with nitre, and washing the residue: this constituted the *Saffron of Mars* (*Crocus Martis*) of ancient pharmacy. The colour of the peroxide of iron varies according to the mode of its formation; it is generally a reddish or yellow-brown powder, which acquires a darkened hue by heat, and is not magnetic. It consists of

		Bucholz	Gay Lussac.	Stromeyer.	Berzelius.	Döbereiner.	Klaproth.
Iron .	1 . 28 . 70 .	70.423	70.27	69.85	69.22	69	67
Oxygen	$1\frac{1}{2}$ . 12 . 30 .	29.577	29.73	30.15	30.78	31	33
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1    40   100	100.000	100.00	100.00	100.00	100	100

It will be observed, that the proportion of oxygen in the protoxide is to that in the peroxide as 1 to 1.5; and, as both these oxides form salts, it will be found that the *proto-salts* are constituted of one proportional of protoxide, and one of acid; and the *per-salts* of one proportional of peroxide, and one and a half of acid. In the combinations of iron with chlorine, the same relative proportions are followed as in the oxides, but the two sulphurets are respectively constituted of one proportional of iron, and one of sulphur, and one and two. Gay-Lussac (*Ann. de Chim. et Phys.*, i., and *Ann. de Chim.*, lxxx.) has detailed some experiments, which he considers as demonstrating the existence of a third definite oxide of iron, intermediate between the above oxides, and composed of iron 100 + oxygen 37.8. Such a compound, he thinks, is obtained by passing steam for a length of time over red-hot iron, and considers it as differing from the true protoxide: this seems, however, very questionable; and the third oxide is rejected by Berzelius, who only admits the oxides above described. Thenard, in describing the oxides of iron (*Traité*, ii., 75, *édit.* 2<sup>e</sup>.), considers the octoëdral and magnetic iron-ores as composed of this deutoxide, and does not allow of the existence of native protoxide of iron. In the present state of the question, however, I should feel rather inclined to view this deutoxide as a mixture of the protoxide and peroxide, than as any definite compound, more especially as the analyses of the native magnetic oxides give variable proportions of oxygen.

*Native Oxides of Iron.* These constitute a very extensive and important class of metallic ores. They vary in colour, depending upon mere texture in some cases; in others, upon the degree of oxydizement. Some are magnetic, and those which contain least oxygen are attracted by the magnet. From them the commercial demands of iron are partly supplied: an outline of this manufacture will be given at

the end of this Section, when the other combinations of the metal have been described. The following are some of the principal mineralogical varieties of the oxides of iron. (1.) *Magnetic iron ore* is generally black, with a slight metallic lustre. It occurs massive and octoëdral. It is often sufficiently magnetic to take up a needle; its specific gravity is 4.5. It occurs chiefly in primitive countries, and is very abundant at Roslagen in Sweden, where it is manufactured into a bar-iron particularly esteemed for making steel. (2.) Another variety of oxide of iron is called *iron-glance*, and *micaceous iron-ore*. It is found crystallized of singular beauty, in the isle of Elba; and occasionally among the volcanic products of Vesuvius and the Lipari Islands. (3.) *Hæmatite*, or red iron-stone: it occurs in globular and stalactitic masses, having a fibrous and diverging structure. In this country, it abounds near Ulverstone in Lancashire; and most of our iron-plate, and wire, is made from it. Sometimes it is of a brown, black, or ochraceous colour. (4.) A fourth variety of oxide of iron is known under the term of *clay-iron-stone*, on account of the quantity of argillaceous earth with which it is contaminated. It is found in masses of different shapes and sizes, and sometimes in small rounded nodules like peas. Some of the globular masses are called *ætites*. The iron-ore of the coal formations of Shropshire, South Wales, Staffordshire, and Scotland, (which, though far from the purest ore found in this country, is the principal source of the cast and bar iron, in ordinary use,) is chiefly a carbonate.

IRON AND CHLORINE unite in two proportions; forming a protochloride and a perchloride of iron, which in atomic composition are analogous to the oxides.

PROTOCHLORIDE OF IRON, ( $fe + c$ .) may be obtained, (1.) by passing muriatic acid gas over red-hot iron-wire or turnings; or (2.) by evaporating a solution of protoxide of iron in muriatic acid to dryness, out of the contact of the air; or (3.) by heating a mixture of iron filings and muriate of ammonia. A brittle gray lamellar substance is thus formed, fusible at a red-heat, and volatile at a higher temperature. It is soluble in water, but insoluble in absolute alcohol. It is decomposed by oxygen at a red-heat; chlorine is evolved, and oxide of iron formed. It consists of

				J. Davy.			
Iron . . .	1	..	28	..	43.7	..	46.57
Chlorine .	1	..	36	..	56.3	..	53.43
	1		64		100.0		100.00

HYDRATED PROTOCHLORIDE OF IRON is obtained in small green crystals, very soluble, and of a styptic taste, by carefully evaporating a solution of protoxide of iron in muriatic acid, which for this purpose is best obtained by the action of equal parts of strong muriatic acid and water, on protosulphuret of iron: sulphuretted hydrogen gas is evolved, and the filtered solution is of a green colour. This is commonly called *protomuriate of iron*.

PERCHLORIDE OF IRON. ( $fe + 1\frac{1}{2}c$ .) When iron-wire is heated in chlorine it burns with a red light, and a compound is formed, volatile at



a heat much below redness, and which condenses in the form of brilliant and iridescent brown scales, soluble in water and alcohol. It consists of

					J. Davy.
Iron . . . .	1 . . . .	28 . . . .	34.2 . . . .	35.1	
Chlorine . . .	$1\frac{1}{2}$ . . . .	54 . . . .	65.8 . . . .	64.9	
	1	82	100.0	100.0	

HYDRATED PERCHLORIDE OF IRON, OR PERMURIATE OF IRON, is obtained by dissolving peroxide of iron in muriatic acid; it forms a deep-brown liquid, which, when concentrated to the consistence of a syrup nearly, and then exposed to cold, yields brown crystals; it is the basis of the *tinctura ferri muriatis* of pharmacy. When decomposed by heat, water, muriatic acid, and perchloride of iron are given off, and the residue is a crystallized compound of peroxide and perchloride of iron. By exposing a solution of the protochloride to air, it passes into the brown perchloride. According to Berzelius, if a solution of the former be exposed for some days to the atmosphere in a tall jar, and a few drops of ammonia be then introduced at different depths, by means of a glass tube, the precipitate near the surface will be green; a little lower, blue; still lower, gray; then of a dirty white; and, at the bottom, quite white, provided the solution has not been so long exposed as to have become oxidized throughout. By saturating a strong solution of muriate of iron with chlorine, Van Mons obtained a brown liquid, which did not give out the odour of chlorine, and tasted astringent, slightly acid, and sweet. After a time, yellow crystals formed, and chlorine was evolved. The crystals soon deliquesced, and could not be obtained a second time.

AMMONIO-MURIATE OF IRON. When muriate of ammonia and peroxide of iron are mixed and exposed to heat in a proper subliming vessel, a yellow sublimate is obtained, which is the *ens veneris* and *flores martiales* of old pharmacy; the *ferrum ammoniatum* of the present *Pharmacopœia*; it consists chiefly of muriate of ammonia, with a small but variable proportion of perchloride of iron. If a compound of the muriate of ammonia and of iron be required for pharmaceutical use, it would be best prepared by adding a solution of perchloride of iron to one of muriate of ammonia, and evaporating to dryness. When such a mixed solution of muriate of ammonia and chloride of iron is set aside to crystallize, it furnishes ruby-coloured cubic crystals, which contain about 2 per cent. of chloride of iron: this is not a definite salt, but apparently a mixture only of the chloride and muriate, and is of variable composition, according to the quantity of chloride present.

THE CHLORATES OF IRON have not been satisfactorily examined.

PROTIODIDE OF IRON, (*fe + i,*) is formed by digesting iron-turnings or wire with iodine in water, taking care to have excess of metal present: a green solution is obtained, which affords green tabular crystals of *protiodide*, and which by evaporation out of contact of air leaves a deliquescent residue, which, when fused, acquires a gray colour. It is soluble in water and alcohol, and the solution rapidly absorbs oxygen, and deposits peroxide of iron, unless metallic iron be present, so that to preserve it unchanged some pieces of clean iron-wire should be immersed

in it. This solution has been very advantageously employed in medicine by Dr. A. T. Thomson.

THE PERIODIDE OF IRON has not been examined, or, at least, not satisfactorily described: according to Berzelius, the brown powder which falls on exposing the solution of the protiodide to air is a *hydrated sub-periodide*. According to Mr. Squire it is merely peroxide of iron, and no periodide exists.

IODATE OF IRON. Iodate of potassa throws down a yellowish precipitate in solution of protosulphate of iron, and a white precipitate in solution of perchloride of iron. (Pleischl.)

PROTOBROMIDE OF IRON. When bromine vapour is passed over red-hot iron-wire, a yellow fusible bromide is obtained, readily soluble in water. (*Ann. de Chim. et Phys.*, xxxiii., 331.)

FLUORIDES OF IRON. When iron is digested in hydrofluoric acid, a solution is obtained, which affords small quadrangular tabular crystals; they are colourless, and difficultly soluble in water. Heated rapidly in the air, this salt is decomposed; but if its water of crystallization be slowly and carefully expelled, it then may be fused into a true *fluoride of iron*. When hydrated peroxide of iron is dissolved in hydrofluoric acid, it forms a colourless solution, which yields flesh-coloured crystals, slowly soluble in water. Ammonia throws down a yellow precipitate, which is a subfluoride: a double *fluoride of potassium and iron* is obtained in colourless crystals, when a mixed solution of those fluorides is evaporated. (Berzelius.)

PROTONITRATE OF IRON. When very dilute nitric acid (sp. gr. 1.16) is digested upon iron-filings, little gas is evolved, and the liquid assumes an olive-brown colour from the nitric oxide which it contains, but exposed to the air it becomes pale-green in consequence of the escape of that gas; the alkalis produce a green precipitate in this solution: it cannot be obtained in crystals by the usual process, and passes into pernitrates by exposure to air. It may, however, according to Thomson, be crystallized by evaporation in an exhausted receiver over sulphuric acid; it then forms transparent rhomboidal crystals of a light-green colour, composed of 1 atom of protoxide of iron, 1 of nitric acid, and 7 of water. When protosulphuret of iron is dissolved in dilute nitric acid sulphuretted hydrogen escapes, and a green solution of protonitrate of iron is obtained, which, when gently heated, speedily becomes brown, in consequence of the formation of peroxide.

PERNITRATE OF IRON. Nitric acid, diluted with a very little water, acts violently on iron and peroxidizes it, a vast quantity of gas being at the same time generated, which consists of a mixture of nitrous and nitric oxides; and a solution is formed of a reddish-brown colour, containing *pernitrate* of iron, and affording a brown precipitate to the alkalis. When evaporated, a brown deliquescent mass remains, soluble in water and alcohol. It is decomposed at a red-heat, and peroxide of iron remains. If this solution be mixed with excess of carbonate of potassa, the precipitate at first thrown down is redissolved by the alkali, and a deep-brown liquid obtained, called in our *Pharmacopœia*, *Liquor ferri alkalini*. It has long been known in Germany under the name of "Stahl's alkaline tincture of iron."

PROTOSULPHURET OF IRON. ( $fe + s.$ ) 1. When sulphur is dropped upon red-hot iron-wire, or fused with iron-filings, a compound is obtained, which, after having been heated to expel excess of sulphur, is perfectly soluble in dilute sulphuric acid, with the evolution of pure sulphuretted hydrogen, and which is a protosulphuret of iron. 2. White-hot iron, exposed to a jet of sulphur vapour, burns in it, and runs down into the protosulphuret. 3. It is formed by exposing pure yellow pyrites, or bisulphuret of iron, to a red-heat; or, 4, by passing dry hydrogen gas over powdered iron pyrites, heated to redness in a glass or porcelain tube. 5. It is thrown down on adding hydrosulphuret of ammonia to solution of protosulphate of iron. 6. By the mutual action of iron-filings and powdered sulphur made into a paste with water. Protosulphuret of iron is of a yellowish or bronze colour, and influences the magnet. It consists of

					Hatchett.	Berzelius.	Proust.
Iron . . .	1	..	28	..	63.5	..	62.5
Sulphur . .	1	..	16	..	36.5	..	37.5
	<hr/>		<hr/>		<hr/>		<hr/>
	1		44		100.0		100.0

BISULPHURET OF IRON, ( $fe + 2s.$ ) is formed, according to Berzelius, when the black sulphuret is well mixed with half its weight of sulphur, and subjected to a high temperature, which, however, must be below redness: a bulky, dark-yellow metallic powder is the result, which is not attracted by the magnet, and insoluble in dilute sulphuric and muriatic acid. A similar compound is obtained by passing a current of sulphuretted hydrogen over peroxide of iron at a temperature just below redness. If natural crystals of oxide of iron be subjected to this process, they are converted without change of form into the bisulphuret. When exposed to heat in close vessels it loses half its sulphur, and becomes protosulphuret. We have two interesting cases of the formation of this sulphuret in the humid way. The one, described by Mr. Hatchett as occurring in the Mere of Diss, in Norfolk, (*Phil. Trans.*, 1797); the other, by Mr. Pepys, in the *Geological Transactions*, vol. i., p. 399, and taking place in the bones of mice which had fallen into a solution of sulphate of iron. Bisulphuret of iron consists of

					Berzelius.	Hatchett.	Bucholz.
Iron . . .	1	..	28	..	46.6	..	49
Sulphur . .	2	..	32	..	53.4	..	51
	<hr/>		<hr/>		<hr/>		<hr/>
	1		60		100.00		100.

*Native Sulphurets of Iron.* Mr. Hatchett's experiments, above quoted, show that the ore of iron, called *magnetic pyrites*, is a protosulphuret of iron, and that *common pyrites* is a bisulphuret; the results of his analysis of these ores are given in the preceding paragraphs. Common pyrites is found, massive and crystallized, in a variety of forms, derived from a primitive cube; it often occurs in radiated nodules, which, when rolled amongst the shingles upon the sea-beach, are sometimes erroneously supposed to be of meteoric origin, and are called *thunder-bolts*. This mineral is of different shades of brass-yellow. The principal use of pyrites is in the formation of *sulphate of iron*, or *green vitriol*, for which purpose the ore is gently roasted and exposed to air and moisture.

Some varieties are spontaneously decomposed, and furnish this salt, and when in large masses, generate heat enough to become ignited: in this way beds of coal have been set on fire in consequence of the absorption of oxygen by their contained pyrites. Pyrites has also been used as a source of sulphur in the production of sulphuric acid.

SESQUISULPHURET OF IRON, ( $fe + 1\frac{1}{2} S$ .) This compound is formed by passing sulphuretted hydrogen over peroxide of iron at a temperature not exceeding  $212^{\circ}$ ; or by the action of the same gas upon the hydrated peroxide at common temperatures. According to Proust, it may be formed by the action of sulphur on the protosulphuret at a very low red-heat: he states it to be magnetic, which Berzelius denies. It is formed in the humid way, by adding neutral persulphate of iron, drop by drop, to a solution of an alkaline hydrosulphuret; it then falls as a black powder, which cannot be dried in the air without change. It corresponds in composition with the peroxide, and consists of

				Berzelius.	Proust.	Bucholz.					
Iron . . .	1	..	28	..	53.8	..	52.92	..	52.64	..	52.07
Sulphur .	$1\frac{1}{2}$	..	24	..	46.2	..	47.08	..	47.36	..	47.93
	1		52		100.0		100.00		100.00		100.00

DISULPHURET OF IRON, ( $2fe + S$ .) is formed, according to Arfwedson, by passing a current of hydrogen gas over anhydrous protosulphate of iron, heated to redness: sulphurous acid, water, and sulphuretted hydrogen, are evolved, and 46.47 *per cent.* of the above compound remain. This is probably a definite compound of 1 atom of iron + 1 atom of protosulphuret of iron.

TETRA-SULPHURET OF IRON, ( $4fe + S$ .) is also described by Arfwedson as a definite sulphuret; he obtained it by passing a current of hydrogen over anhydrous subpersulphate (disulphate of the peroxide) of iron. These compounds are gray and pulverulent; and they both evolve mixtures of hydrogen and sulphuretted hydrogen when dissolved in dilute sulphuric acid.

HYPOSULPHITE OF PROTOXIDE OF IRON, ( $Fe + \underline{S}$ .) is obtained by dissolving finely-divided metallic iron in sulphurous acid; a solution is obtained at first brown, but becoming green, and no gas is evolved: it does not crystallize, and is decomposed by exposure to air. When sulphuric or muriatic acids are added to its solution, sulphurous acid is evolved, and sulphur precipitated. The solution of this hyposulphite furnishes one of the best instances of a pure protosalt of iron; and by keeping a few filings of iron in it, it may be retained in this state. It gives a perfectly-white precipitate with the ferrocyanuret of potassium, if dilute, infusion of galls does not immediately discolour it.

PROTOSULPHITE OF IRON, ( $Fe + \hat{S}$ .) has not been accurately examined.

HYPOSULPHATE OF PROTOXIDE OF IRON is formed by mixing a solution of hyposulphate of baryta with protosulphate of iron: the filtered solution furnishes green prismatic crystals, easily soluble, and containing 29.54 *per cent.* of water of crystallization.

SULPHATES OF IRON. Sulphuric acid forms salts with both the oxides of iron, and we have accordingly a *protosulphate*, and a *persulphate* of iron; the latter is sometimes incorrectly termed a *sesquisulphate*, because

1 proportional of peroxide of iron combines with  $1\frac{1}{2}$  of sulphuric acid ; but as the peroxide of iron contains 1 atom of iron united to  $1\frac{1}{2}$  of oxygen ; the acid of the salt is the proper equivalent to that of the oxygen in the oxide.

PROTOSULPHATE OF IRON, (Fe + S',) is the *copperas* and *green vitriol* of commerce, and is often prepared by exposing roasted *pyrites* or *bisulphuret of iron* to air and moisture, in which case the salt is impure. It is usually formed for medicinal and chemical purposes, by dissolving iron-filings, or turnings, in dilute sulphuric acid, filtering and evaporating the solution, and setting it aside to crystallize. It is also obtained, perfectly free from persulphate, by acting upon the artificial *protosulphuret* of iron by dilute sulphuric acid. This salt forms green crystals in the form of oblique rhombic prisms, (Brooke, *Ann. of Phil.*, 2nd series, vi. 120,) of a styptic taste, reddening vegetable blues ; and including, according to Thomson, seven, or, according to Mitscherlich, six proportionals of water. The solubility of 1 part of this salt at different temperatures is, according to Brandes and Firnhaber, as follows, (Gmelin.)

Temperature	50°	59°	75°	92°	115°	140°	183°	194°	212°
Water	. . 1.64	. . 1.43	. . 0.87	. . 0.66	. . 0.44	. . 0.38	. . 0.37	. . 0.27	. . 0.30

The solution is pale-green, and absorbs nitric oxide gas, acquiring a deep-brown colour ; it also absorbs chlorine, and muriatic acid is formed, and the iron becomes peroxidized ; so that water is here decomposed. It is insoluble in alcohol and in sulphuric acid, both of which deprive the crystals of water, and precipitate the salt from its solutions in the form of a white powder.

Exposed to air and moisture, the protosulphate of iron gradually absorbs oxygen, and is partly converted into a persulphate. It may also be converted into persulphate by nitric acid. When heated, it fuses in its water of crystallization, and at a high temperature evolves anhydrous sulphuric acid, peroxide of iron remaining in the vessel : by this process sulphuric acid used formerly to be prepared, and the residue was known under the name of *caput mortuum vitrioli* or *colcothar*. Hence, also, it is, that sulphate of iron is often used as a substitute for sulphuric acid, to separate weaker acids from their bases, at high temperatures. If the green crystals of this salt be carefully exposed to a temperature of about 300°, they crumble down into a white powder, composed of one proportional of dry sulphate, and one of water. Protosulphate of iron (anhydrous) consists of

						Berzelius.		Wenzel.	
Protoxide of iron	1	. .	36	. .	47.4	. .	47.07	. .	42.17
Sulphuric acid	. 1	. .	40	. .	52.6	. .	52.93	. .	57.83
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		76		100.0		100.00		100.00

and the crystals are composed of

						Berzelius.	Thomson.	Mitscherlich.
Anhydrous protosulphate of iron	1	. 76	. 54.6	. 54.6	. 55	. 56.08		
Water	. . . . .	. 7	. 63	. 45.4	. 45.4	. 45	. 43.92	
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1	139	100.0	100.0	100	100.00		

The brown powder which falls when solution of protosulphate of iron is heated in the contact of air is, according to Berzelius, a *sub-persul-*

phate, composed of 1 proportional of acid, 4 of peroxide, and 6 of water, or 40 acid + 160 peroxide + 54 water = 254.

*Native Green Vitriol* is frequently found associated with iron pyrites, being produced by its decomposition: it occurs in several of our coal-mines.

PROTOSULPHATE OF IRON AND AMMONIA is a triple salt, the crystals of which contain 8 proportionals of water, and are isomorphous with the ammonia-sulphate of magnesia (Mitscherlich.)

PROTOSULPHATE OF IRON AND POTASSA is obtained by mixing solutions of proportionals of each of the salts; it is of a very pale tint of green, and the crystals contain six proportionals of water (Mitscherlich), five (Thomson.)

PERSULPHATE OF IRON, ( $fe + 1\frac{1}{2}o + 1\frac{1}{2}s'$ .) is obtained by dissolving the moist red oxide in sulphuric acid; or by adding sulphuric acid to a solution of the protosulphate, heating the mixture, and dropping into it nitric acid sufficient to peroxidize the salt. It does not crystallize, but affords, by evaporation, a brown deliquescent mass. It is formed in the mother-waters of the sulphate. Its taste is highly astringent; it is soluble in alcohol; when dry it becomes white. When concentrated sulphuric acid is dropped into a strong solution of this persulphate, it throws it down in the form of a white anhydrous powder. This occasionally occurs in sulphuric acid of commerce, and has been mistaken for sulphate of lead. Persulphate of iron consists, according to Thomson, of

Peroxide of iron . . . .	1	..	40
Sulphuric acid . . . .	$1\frac{1}{2}$	..	60
	1		100

SUBPERSULPHATE OF IRON. When an aqueous solution of protosulphate of iron is exposed to air, or when a small addition of ammonia is made to the persulphate, a brown powder falls, composed, according to Berzelius, of 4 atoms of peroxide of iron and 1 of sulphuric acid: it is, therefore, a *tetrasubpersulphate*.

AMMONIO-PERSULPHATE OF IRON may be obtained in octoëdral crystals, which are colourless, and not unlike alum, by evaporating a mixed solution of sulphate of ammonia and excess of persulphate of iron. This salt, according to Forchammer (*Ann. of Phil.*, v.), is composed of

Persulphate of iron . . . .	2	..	200	..	41.5	..	41.95
Sulphate of ammonia . . . .	1	..	57	..	11.8	..	12.11
Water . . . . .	25	..	225	..	46.7	..	45.94
	1		482		100.0		100.00

When ammonia is cautiously added to a solution of persulphate of iron, and the mixture left to spontaneous evaporation, six-sided prismatic crystals are deposited, composed, according to Maus, (*Poggend*, vol. xi., p. 79,) of

Sulphuric acid . . . . .	49.20
Ammonia . . . . .	10.30
Peroxide of iron . . . . .	23.75
Water . . . . .	16.75
	100.00

PERSULPHATE OF IRON AND POTASSA forms octoëdral crystals much resembling alum in form, colour, and taste. These crystals are occasionally found amongst those of common alum, and are a most inconvenient impurity. They are decomposed by repeated solution in water: they consist, according to Mitscherlich, of

Persulphate of iron	. . .	2	. .	200	. .	39.0
Sulphate of potassa	. . .	1	. .	88	. .	17.4
Water	. . . . .	25	. .	225	. .	43.6
		1		513		100.0

PHOSPHURET OF IRON; DIPHOSPHURET OF IRON, ( $2fe + p$ ), may be formed by dropping phosphorus into a crucible containing red-hot iron-wire; it is a brittle gray compound, and acts upon the magnet. Upon the subject of the magnetic qualities of the sulphuret and phosphuret of iron, the reader is referred to Mr. Hatchett's analysis of the magnetical pyrites. (*Phil. Trans.*, 1804.) It may also be procured by the ignition of a mixture of iron-filings, phosphoric acid, and charcoal-powder; it is very difficultly soluble in the acids. A small portion of this compound is said to be present in all *cold-short iron*. It appears to consist of

				Berzelius.	Pelletier.					
Iron	. . . . .	2	. .	56	. .	77.0	. .	76.805	. .	80
Phosphorus	. .	1	. .	16	. .	22.1	. .	23.195	. .	20
		1		72		100.0		100.000		100

When phosphuretted hydrogen gas is passed over heated iron pyrites a compound is formed, containing 54.92 to 56.87 iron + 45.08 to 43.13 phosphorus. (H. Rose.)

PROTOPHOSPHATE OF IRON ( $Fe + p'$ ) is insoluble, and may be formed by adding solution of phosphate of soda, to protosulphate of iron. The *protophosphate* of iron is at first white, but soon becomes of a pale-blue colour by exposure; it is soluble in most of the acids, from which it may again be precipitated by ammonia.

PERPHOSPHATE OF IRON is a white insoluble precipitate, formed by adding phosphate of soda to persulphate or perchloride of iron: when heated it gives out water and becomes brown. Digested with potassa or soda it is converted into a brown *subperphosphate*.

These phosphates have been analyzed by Vogel, but his results do not accord with theory (*Ann. of Phil.*, xiii., 310), consistently with which the protophosphate should consist of 28 acid + 36 protoxide; and the perphosphate of 42 acid + 40 peroxide.

*Native Protophosphate of Iron* occurs in the form of a blue earthy powder, or it is at first white, and becomes blue by exposure: it also is found in prismatic crystals. The former has sometimes improperly been termed *Native Prussian Blue*, and has been found in alluvial soil: the latter occurs with iron pyrites in Cornwall. The blue crystallized variety analyzed by Stromeyer (*Untersuchungen*, i., 274) afforded

Phosphoric acid	. . . . .	31
Protoxide of iron	. . . . .	41
Water	. . . . .	28
		100

IRON AND CARBON. The different kinds of *cast-iron* and of *steel* contain more or less carbon, which materially affects their properties. The substance termed *Plumbago*, *Graphite*, or *Black Lead*, is generally regarded as a true *carburet of iron* (see p. 463): this is not an uncommon mineral, though rarely found of sufficient purity for the manufacture of pencils: at Borrodale in Cumberland, where it occurs particularly pure, it is imbedded in masses in slate and grauwacke: the coarser kinds and the dust are melted with sulphur for common carpenters' pencils: it is sometimes used in the manufacture of crucibles, and it forms an ingredient in compositions for covering cast-iron, and for diminishing friction in machines. Plumbago is infusible, and burns with great difficulty; its composition was ascertained by Allen and Pepys, by exposing it in the apparatus used for burning the diamond, (p. 469,) to a current of oxygen at a red-heat, and ascertaining the quantity of carbonic acid and of oxide of iron thus produced. They found the average quantity of iron in plumbago to be 5 *per cent.* By long fusion of steel with charcoal Stodart and Faraday obtained a highly-crystalline compound, to which we shall again advert (see STEEL), containing from 5 to 6 *per cent.* of carbon. When pure Prussian blue is decomposed at a red-heat in close vessels, a *carburet of iron* remains, composed of 1 atom of iron and  $1\frac{1}{2}$  of carbon; it is a black pulverulent substance, which at a low heat takes fire in the air, and burns into peroxide of iron, evolving at the same time carbonic acid.

Considerable difficulty attends the accurate analysis of artificial compounds of carbon and iron, in estimating the proportion of the former; this has generally been indirectly effected by ascertaining the quantity of iron, and considering the loss of weight as carbon, a method obviously objectionable. If the action of dilute sulphuric acid be resorted to, a portion of carbon is carried off by hydrogen; the same is the case with muriatic acid; and if nitric acid be used, some carbonic acid may be formed, and artificial tannin is produced.

PROTOCARBONATE OF IRON. ( $\text{Fe} + \text{car}'$ .) Carbonic acid may be combined with the protoxide of iron, by adding carbonate of potassa to solution of protosulphate of iron; a white or greenish precipitate of hydrated *protocarbonate of iron* falls, which, exposed to air, becomes brown, and evolves carbonic acid; so that a dry protocarbonate of iron cannot thus be obtained. Solution of bicarbonate of potassa occasions a white precipitate with sulphate of iron, part of which is redissolved on adding excess of the carbonated alkali. When carbonic acid in aqueous solution is digested with iron-filings, a colourless solution of the protocarbonate is obtained: it is not an uncommon ingredient in mineral waters.

The protocarbonate of iron consists of

Protoxide of iron . . . .	1	..	36	..	62
Carbonic acid . . . .	1	..	22	..	38
	1		58		100.

*Native Protocarbonate of Iron*, or *Spathose Iron Ore*, occurs in Germany, and in some parts of Cornwall, crystallized in imperfect rhomboids. Its colour is yellowish, or brownish-gray. It generally contains manganese, lime, and a trace of magnesia. A specimen of this mineral



from Eulenloh in Bareuth, analyzed by Bucholz (*Gehlen's Journ.*, i., 231), contained carbonic acid 36, protoxide of iron 59, lime 3, water 2. These components indicate that this mineral consists essentially of protocarbonate of iron, composed as above. The *clay iron ore* of our coal districts, from which English iron is chiefly obtained, is an impure *protocarbonate of iron*. Previous to reduction, it is reduced by heat, to the state of oxide, as will appear from the account of the manufacture of iron, at the end of this section.

PERCARBONATE OF IRON has not been obtained in a separate state; for the protocarbonate, whilst drying, exposed to air, loses carbonic acid, and becomes peroxide. When bicarbonated alkalis are digested with recently-precipitated peroxide of iron, triple salts are formed.

IRON AND CYANOGEN. These substances give rise to several important compounds, in which they exist either combined in various proportions, or as a *basis*, in union with other bodies.

PROTOCYANURET OF IRON is obtained according to Berzelius in the form of a gray powder, by gently heating ammonio-cyanuret of iron (Ferrocyanate of Ammonia) out of the contact of air. It falls in the form of a white *hydrate* when a pure protosalt of iron is decomposed by ferrocyanuret of potassium; but in this state it is not permanent, and quickly passes into Prussian blue by the absorption of oxygen. In its dry state, it consists of

Iron . . .	1	..	28	..	51.8	Iron . . .	51.8
Carbon . . .	2	..	12	..	22.3	} Cyanogen . . .	48.2
Nitrogen . . .	1	..	14	..	25.9		
	<u>1</u>		<u>54</u>		<u>100.0</u>		<u>100.0</u>

FERROCYANURETS. Protoxide of iron, which we may call *ferrocyanogen*, combines with a variety of other metallic cyanurets, forming double cyanurets, or *ferrocyanurets*, and they are generally so constituted as to contain 1 equivalent of the ferrocyanogen combined with 2 equivalents of the other cyanuret: their elements, therefore, are in such a ratio, that if the metals were converted into *protoxides* at the expense of water, the hydrogen would just suffice to form hydrocyanic acid with the cyanogen; or, in other words, *one* equivalent of the respective ferrocyanurets would decompose *three* equivalents of water.

These *ferrocyanurets* are decomposed by heat with various phenomena. 1. The ferrocyanogen evolves nitrogen and becomes converted into bicarburet of iron, which remains mixed with the basic cyanuret: this is the case with *ferrocyanuret of potassium*. 2. The cyanogen of both the cyanurets is decomposed, nitrogen evolved, and metallic bicarburets of iron and of the basic metal are formed, as with *ferrocyanuret of lead*. 3. The basic cyanuret evolves cyanogen, and is reduced, as in the case of *ferrocyanuret of silver*.

FERROCYANURET OF POTASSIUM; FERROCYANATE OF POTASSA; PRUSSIAN BLUE OF POTASSA. (*fe + cy*) + 2(*po + cy*.) When *Prussian blue* is boiled with potassa it is decomposed; it loses its blue colour; oxide of iron is separated; and on filtering and evaporating the solution, crystals of the above compound are obtained. It is best formed by adding powdered Prussian blue (previously heated with a dilute sulphuric acid

composed of one part of acid and five of water, and afterwards washed) to a hot solution of potassa, as long as its colour is destroyed. It is largely prepared as an article of commerce, chiefly for the use of calico-printers, by the following process:

“Into an egg-shaped *iron* pot, brought to moderate ignition, project a mixture of good pearl-ash and dry animal matters\*, of which hoofs and horns are best, in the proportion of two parts of the former to five of the latter. Stir them well with a flat *iron* paddle. The mixture, as it calcines, will gradually assume a pasty form, during which transition it must be tossed about with much manual labour and dexterity. When the conversion into a chemical compound is seen to be completed by the cessation of the fetid animal vapours, remove the pasty mass with an iron ladle. If this be thrown, while hot, into water, some of the prussic acid will be converted into ammonia, and of course the usual product diminished. Allow it to cool, dissolve it in water, clarify the solution by filtration or subsidence, evaporate, and, on cooling, yellow crystals of the ferroproussiate of potash will form. Separate these, redissolve them in hot water, and, by allowing the solution to cool very slowly, larger and very regular crystals may be had.” (Ure’s *Dictionary*.)

This salt, by careful evaporation, forms permanent lemon-yellow crystals, of a specific gravity of 1.83: they are more soluble in hot than cold water, insoluble in alcohol, and of a cooling saline taste. Dr. Ure states, that water at 60° takes up about one-third, and at 212° its own weight of this salt. The large crystals have a peculiar toughness, and the thin ones are somewhat flexible and elastic: their forms have been described by Mr. Levy and Mr. Brooke. (*Quart. Jour.*, xv., 288; *Ann. of Phil.*, N. S., vi., 41.) They are four-sided tables, derived from a primary octoëdron. When moderately heated this salt loses its colour, and crumbles down into a white powder, parting with about 13 *per cent.* of water. The crystals retain their figure till upon the verge of ignition. It is decomposed in a retort at a red-heat, hydrocyanic acid and ammonia are evolved, and the residue consists of charcoal, potassa, and iron. Exposed to a red-heat in a platinum crucible, a brown mass is obtained, which, washed with water, deposits a gray cyanuret of platinum. The aqueous solution furnishes, on evaporation, hydrocyanate of potassa, and a large quantity of transparent colourless prismatic crystals. (Thenard.) Boiled with dilute sulphuric or muriatic acids, hydrocyanic acid is given out, and a white precipitate formed similar to that which the salt produces in a solution of protosulphate of iron.

Neither sulphuretted hydrogen, the hydrosulphurets, the alkalis, nor tincture of galls, produce any precipitate in solutions of this salt. Red oxide of mercury decomposes it at a moderate heat, peroxide of iron and metallic mercury are precipitated, and *cyanuret of mercury* formed; so that the iron is peroxidized at the expense of the oxide of mercury.

When a solution of this salt forms insoluble precipitates in metallic solutions, the nature of the metal present may often be judged of by the character and colour of the precipitate, as indicated by the following table:

\* Iron-filings are occasionally added to the above mixture.

METAL.	SOLUTION.	PRECIPITATE.
MANGANESE	Neutral protomuriate	White
IRON . .	Neutral protosulphate	White or pale blue
Ditto . .	Permuriate	Prussian blue
ZINC . .	Muriate	Yellowish white
TIN	Acid protomuriate	White, then yellow and bluish
Ditto . .	Acid permuriate	Pale yellow
CADMIUM . .	Muriate	White
COPPER . .	Protomuriate	Lilac
Ditto . .	Pernitrate	Deep brown
LEAD . . .	Nitrate	White
ANTIMONY .	Tartrate of antimony and potassa	0
BISMUTH . .	Tartrate of bismuth and potassa	0
COBALT . .	Muriate	Pale green
URANIUM . .	Sulphate	Deep brown
TITANIUM . .	Acid muriate	Deep blue (from acid)
Ditto . .	Neutral sulphate	Sap green
CERIUM . .		White
TELLURIUM		
ARSENIC . .	White oxide	
Ditto . .	Arsenic acid	
NICKEL . .	Sulphate	Gray
MERCURY . .	Acid nitrate	Greenish white
Ditto . .	Acid pernitrate	Ditto
Ditto . .	Corrosive sublimate	White
RHODIUM . .		0
PALLADIUM	Muriate	Olive
SILVER . .	Nitrate	Cream-colour
GOLD . . .	Muriate	0
PLATINUM .	Ditto	Yellow

Various opinions have been entertained with regard to the proximate composition of the salt we have been describing. In its crystalline form it is, according to Berzelius, a *hydrated ferrocyanuret of potassium*, and I have adopted this as the simplest view of its constitution; that is, as consisting, in its *anhydrous* state, of 1 atom of cyanuret of iron, combined with 2 atoms of cyanuret of potassium. In this state, therefore, its ultimate elements are

						Robiquet.
Iron . . . .	1	..	28	..	15.	.. 14.42
Potassium . .	2	..	80	..	43.	.. 41.36
Cyanogen . .	3	..	78	..	42.	.. 42.91
	<u>1</u>		<u>186</u>		<u>100.</u>	<u>100.00</u>

These elements are equivalent to

Cyanuret of Iron . . . .	1	..	54	..	29
Cyanuret of Potassium . .	2	..	132	..	71
	<u>1</u>		<u>186</u>		<u>100</u>

and the *hydrated, or crystallized ferrocyanuret*, will consist of

				Ure.	Döbereiner.
Anhydrous Ferrocyanuret of Potassium	1	. 186	. 87.5	. 87.12	. 88
Water . . . . .	3	. 27	. 12.5	. 12.88	. 12
	<u>1</u>	<u>213</u>	<u>100.0</u>	<u>100.00</u>	<u>100.</u>

But another view of the nature of this salt, in its hydrated form, has been taken by some chemists, founded upon the original experiments of

Mr. Porrett (*Phil. Trans.*, 1814), and perfectly consistent with its atomic constitution. It will be observed that 1 atom of the anhydrous ferrocyanuret is combined with *three* atoms of *water*, the *oxygen* of which is obviously just that required to convert the iron and the potassium into protoxides, and the *hydrogen* to convert the cyanogen into hydrocyanic acid; so that viewed in this way, the salt may be regarded as composed of

Hydrocyanate of Protoxide of Iron . . . . .	1	. .	63	. .	29.6
,, of Potassa . . . . .	2	. .	150	. .	70.4
	<hr style="width: 100%; border: 0.5px solid black;"/>		213		<hr style="width: 100%; border: 0.5px solid black;"/>
	1				100.0

But Mr. Porrett conceived the protoxide of iron to be so combined with the whole of the hydrocyanic acid, as to constitute a distinct acid, which he termed ferruretted cyanic, or *ferrochyazic* acid (from the initial letters of carbon, hydrogen, and azote.)

FERROCHYAZIC ACID; HYDROCYANOFERRIC ACID (of Gay Lussac); HYDROFERROCYANIC ACID; FERROCYANIC ACID. (*fe + o*) +<sub>3</sub> (*cy + h.*) This acid may be obtained according to Porrett as follows: Dissolve 58 grains of crystallized tartaric acid in alcohol, and pour the solution into a phial containing 50 grains of ferrocyanate of potassa dissolved in 3 drachms of warm water; by these means, the potassa is precipitated in the state of supertartrate, and the ferrochyazic acid remains dissolved in the alcohol, from which it may be obtained, by careful evaporation, in small cubic crystals (*Ann. of Phil.*, Sept. 1818); or the solution of ferrocyanuret of barium may be decomposed by sulphuric acid, so as exactly to abstract the baryta in the form of sulphate. Berzelius recommends the decomposition of recently-precipitated ferrocyanuret of lead or copper diffused through water, by sulphuretted hydrogen, filtering, and getting rid of the excess of sulphuretted hydrogen, which would spoil the air-pump, by a little ferrocyanuret of lead: the solution should ultimately be rapidly filtered, and evaporated in vacuo over sulphuric acid. A white residue remains, which, when dissolved in water is sour, inodorous, and yields Prussian blue with a persalt of iron; it dissolves the alkaline carbonates with effervescence, and yields *ferrocyanurets*. Its aqueous solution, when exposed to light and air, gradually deposits Prussian blue; and, when boiled, deposits white protohydrocyanate of iron. Subjected to destructive distillation it yields hydrocyanic acid, hydrocyanate, and carbonate of ammonia, and leaves carburet of iron. This acid consists, according to Berzelius (and Porrett?), of

Protoxide of Iron . . . . .	1	. .	36	. .	30.8
Hydrocyanic Acid . . . . .	3	. .	81	. .	69.2
	<hr style="width: 100%; border: 0.5px solid black;"/>		117		<hr style="width: 100%; border: 0.5px solid black;"/>
	1				100.0

and the crystallized ferrocyanuret of potassium *may* be regarded as an anhydrous disalt of this acid, or as consisting of

Hydroferrocyanic Acid . . . . .	1	. .	117	. .	55
Potassa . . . . .	2	. .	96	. .	45
	<hr style="width: 100%; border: 0.5px solid black;"/>		213		<hr style="width: 100%; border: 0.5px solid black;"/>
	1				100.

FERROCYANATE OF AMMONIA. When ferrocyanuret of lead is diffused through water, holding carbonate of ammonia in solution, or when

Prussian blue is digested in solution of ammonia, the filtered liquors yield small yellow octoëdral crystals, apparently composed of

Hydroferrocyanic Acid	1	..	117	..	77.5
Ammonia . . . . .	2	..	34	..	22.5
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		151		100.0

FERROCYANURET OF SODIUM.  $(fe + cy) + 2(so + cy)$ . This salt is obtained by boiling Prussian blue with caustic soda. Its solution yields hydrated yellow prismatic crystals, soluble in 4.5 of water at 55°, and insoluble in alcohol. They effloresce, and lose by drying 39 per cent. of water.

FERROCYANURET OF BARIUM  $(fe + cy) + 2(ba + cy)$ , is best obtained by mixing boiling-hot solutions of 1 part of chloride of barium and 2 of crystals of pure cyanuret of potassium: as they cool, small yellow rhomboidal prisms are deposited, and the mother-liquor yields more by evaporation. The salt requires 100 parts of boiling water and 1920 of cold water for its solution. The crystals contain 18 per cent. of water, of which the greater part may be expelled by heat.

FERROCYANURET OF STRONTIUM  $(fe + cy) + 2(str + cy)$  is formed by boiling a mixture of Prussian blue and hydrate of strontia in water: it forms yellow crystals soluble in 4 parts of cold water.

FERROCYANURET OF CALCIUM.  $(fe + cy) + 2(cal + cy)$ . When hydrate of lime and Prussian blue are boiled in water, and the resulting solution filtered and evaporated to the consistence of syrup, it yields large lemon-yellow four-sided prisms which effloresce in a warm atmosphere, and at 100° lose nearly 40 per cent. of water, retaining about 2 per cent. which cannot be separated without decomposing the salt.

FERROCYANURET OF MAGNESIUM crystallizes in small deliquescent tables.

FERROSESQUICYANURETS. A *sesquicyanuret of iron*, or a compound of 1 atom of iron and 1½ of cyanogen,  $(2fe + 3cy)$ , cannot be obtained in an insulated state; but, such a compound acts the same part as the protocyanuret of iron in regard to basic cyanurets, and produces a class of definite compounds which have been termed *ferrosesquicyanurets*. (L. Gmelin.)

FERROSESQUICYANURET OF POTASSIUM. When chlorine is passed through a solution of ferrocyanuret of potassium till it ceases to precipitate Prussian blue from the *persalts* of iron, and the fluid then filtered and slowly evaporated, it furnishes small prismatic crystals, which, purified by a second solution, assume a ruby-red colour; they are anhydrous, and require 3.8 parts of cold water for solution, and are nearly insoluble in alcohol. Although this salt occasions no change in solutions of iron containing the peroxide only, it is *a most delicate test of the protoxide of that metal*. This salt (doubling the equivalents, to avoid fractions) is constituted of

					L. Gmelin.
Iron . . . . .	2	..	56	..	17.22
Potassium . . . . .	3	..	120	..	35.65
Cyanogen . . . . .	6	..	156	..	49.00
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		332	100.0	101.87

Or, of	2 equivalents of sesquicyanuret of iron	$(67 \times 2) = 134$	..	40.4
	3 - - - cyanuret of potassium	$(66 \times 3) = 198$	..	59.6
		332		100.0

The *ferrosesquicyanurets of sodium, barium, and calcinm*, may be obtained by the same process, care being taken to avoid excess of chlorine, which is apt to react upon the salt. Solution of the ferrosesquicyanuret of potassium throws down the following metals, of the annexed colours:—

Titanium . . .	Brownish yellow.	Silver . . .	Orange-yellow.
Uranium . . .	Reddish brown.	Mercury . . .	Yellow (both oxides.)
Manganese . . .	Brownish gray.	Tin . . .	White.
Cobalt . . .	Dark red-brown.	Zinc . . .	Orange.
Nickel . . .	Yellowish brown.	Bismuth . . .	Yellow-brown.
Copper . . .	Dirty yellow-brown.		

**FERROSESQUICYANIC ACID.** When ferrosesquicyanuret of potassium is added to a solution of lead, no immediate precipitation ensues, but, after a time, brown crystals of *ferrosesquicyanuret of lead* are deposited. When these are dissolved in water and decomposed by sulphuretted hydrogen, the filtered solution, which is of a red colour, yields, on evaporation, brown crystals, which are acid, and which bear the same relation to ferrosesquicyanogen, as the corresponding product of the ferrocyanuret of lead does to ferrocyanogen.

**FERROSESQUICYANURET OF IRON: PRUSSIAN BLUE.** This celebrated pigment was accidentally discovered by Diesbach, a colour-maker at Berlin, in the year 1710: the first description of the mode of preparing it is given by Woodward in the *Philosophical Transactions* for 1724. It is usually made as follows. Equal parts of carbonate of potassa and some animal substance, such as dried blood, or horn-shavings, are heated red-hot, in a crucible, for half an hour, and six or eight parts of water are poured upon the mixture when it has quite cooled. The solution, which used to be called *lixivium sanguinis*, is filtered and found to contain *hydrocyanate of potassa*, along with carbonate of potassa, and some other products. It is mixed with a solution containing two parts of alum and one of protosulphate of iron; a precipitate falls, at first of a dingy-green hue, but which, by copious washings with very dilute muriatic acid, acquires a fine blue tint.

At present, Prussian blue is prepared of different degrees of purity, by precipitating solutions of peroxide of iron by ferrocyanuret of potassium, various additions being made to it according to the purposes for which it is required. *Pure Prussian blue* is obtained by adding a solution of ferrocyanuret of potassium to persulphate of iron, thoroughly washing the precipitate, first with water slightly acidulated by sulphuric acid, and then with pure water, and ultimately drying it in a warm place. It is of a peculiarly rich and intense blue, with a copper tint upon its surface: it is insipid, inodorous, insoluble in water, in alcohol, and in dilute acids. Concentrated sulphuric acid forms with it a white pasty mass, from which water again separates it unaltered; nitric acid decomposes it; and concentrated muriatic acid abstracts part of its iron. Sulphuretted hydrogen, and iron and zinc filings render it white, in consequence of the abstraction of part of its cyanogen. The alkalis

decompose it with the phenomena already described. It is extremely hygrometric, and after having been well dried, speedily attracts moisture. When subjected to destructive distillation, it yields a little water and hydrocyanate of ammonia, and then carbonate of ammonia, and a black carbonaceous mass remains in the retort.

Prussian blue is manifestly a compound of cyanogen and iron, and various views have been taken of its atomic constitution, according as it has been considered a cyanuret, or a hydrocyanate; that is, as containing or not containing elementary water. From the researches of Berzelius, it appears, if considered as anhydrous, or merely retaining adventitious water, to be constituted of

Sesquicyanuret of iron . . . . .	4		268		62.2
Cyanuret of iron . . . . .	3		162		37.8
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		430		100.0

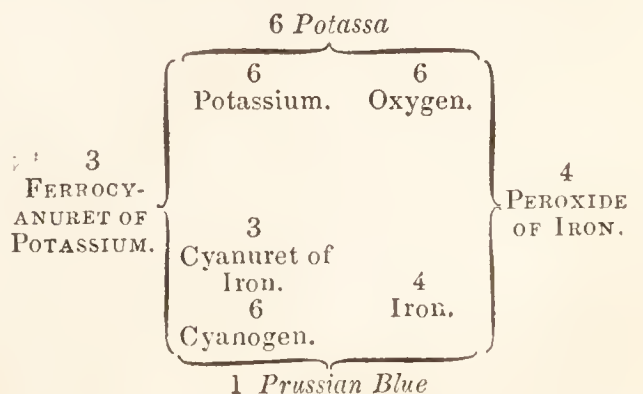
Or, of

Iron . . . . .	7		196		45.5
Cyanogen . . . . .	9		234		54.5
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		430		100.0

The *ultimate elements*, therefore, of anhydrous Prussian blue, are

Iron . . . . .	7		196		45.5
Carbon . . . . .	18		108		25.2
Nitrogen . . . . .	9		126		29.3
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		430		100.0

Assuming, then, Prussian blue to be a compound of 4 atoms of sesquicyanuret of iron, and 3 of cyanuret of iron, we see why it is produced by the action of ferrocyanuret of potassium, (consisting of cyanuret of potassium and cyanuret of iron,) upon the salts of *peroxide* of iron: for an interchange of elements takes place between the cyanuret of potassium and *peroxide* of iron, by which potassa and *sesquicyanuret* of iron are formed. Let us suppose (to avoid fractions) that 3 atoms of ferrocyanuret of potassium (containing 6 atoms of cyanuret of potassium and 3 of cyanuret of iron) act upon 4 atoms of peroxide of iron (containing 4 atoms of iron and 6 of oxygen). In this case, the 6 of potassium (in the ferrocyanuret) combine with the 6 of oxygen (in the peroxide of iron) to form 6 atoms of potassa; and the 4 of iron (in the peroxide) unite to the 6 of cyanogen (in the cyanuret of potassium) to form 4 atoms of *sesquicyanuret of iron*, which, by combining with the 3 of *cyanuret of iron*, (left by the ferrocyanuret of potassium) form *Prussian blue*. The whole result will, perhaps, be more explicit in the annexed diagram, which shows that the iron of the peroxide takes the place of the potassium of the ferrocyanuret. (The annexed *numbers* refer to atoms or equivalents, as will be evident from the foregoing tables of composition.)



blue, but that when it exchanges elements with ferrocyanuret of potassium, *protocyanuret* of iron and not *sesquicyanuret*, must be the result. When, on the other hand, *ferrosesquicyanuret of potassium* is mixed with a *protosalt* of iron, potassa, and cyanuret of iron are the new products; the former unites with the acid previously in combination with the protoxide, and the cyanuret of iron is partly precipitated, and partly unites to the sesquicyanuret of iron contained in the ferrosesquicyanuret of potassium, to form Prussian blue: this will be evident from the annexed diagram, referring at the same time to the above tables of the composition of Prussian blue, and of the ferrosesquicyanuret of potassium.

**SOLUBLE PRUSSIAN BLUE.** It is often remarked, that under certain circumstance of precipitation, Prussian blue becomes apparently soluble in water; this is especially the case when a persalt of iron is added to excess of a solution of ferrocyanuret of potassium. In this case, a compound is formed between the Prussian blue and the ferrocyanuret, soluble in pure water, but insoluble in saline solutions; accordingly, as soon as the salts are washed out of the precipitate, it begins to dissolve in the water. This compound, according to Berzelius (*Ann. de Chim. et Phys.*, li.), consists of 1 atom of ferrocyanuret of potassium and 1 of Prussian blue.

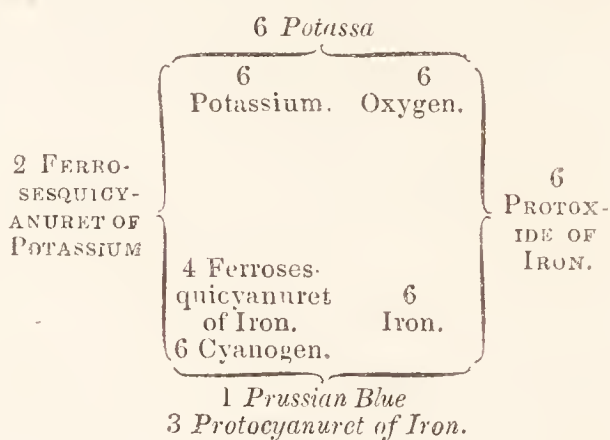
**PROTOSULPHOCYANURET OF IRON.** (*fe + sulcy.*) The sulphocyanic acid dissolves iron with the evolution of hydrogen, and a pale-green solution is obtained, which may be evaporated to dryness in vacuo, but deposits a yellow sediment on exposure to air.

**PERSULPHOCYANURET OF IRON.** (*fe + 1½ sulcy.*) This compound may be obtained in the form of a deliquescent uncrystallizable mass, of a red colour, by dissolving hydrated peroxide of iron in sulphocyanic acid, and carefully evaporating to dryness. When sulphocyanic acid is added to any soluble persalt of iron, it produces a very characteristic red tint, and thus applied, is a delicate and useful test.

**PROTOBORATE OF IRON** is an insoluble powder, obtained by adding a solution of borate of soda to one of protosulphate of iron.

**PERBORATE OF IRON** is of a yellow colour, and insoluble. It is formed by adding borate of soda to persulphate of iron: it is vitrifiable at a high heat. When hydrogen is passed over borate of iron, heated red-hot in a porcelain tube, it is converted into a *boruret of iron*, consisting of 77.43 iron, 22.57 boron? (Lassaigne.)

**ALLOYS OF IRON.** *Iron and Potassium* form a white soft alloy which effervesces in water. When a mixture of charcoal, iron-filings, and magnesia, is exposed to its fusing heat, the resulting globule contains traces of *magnesium*. With lime no analogous effect ensues. The alloy of *iron and manganese* is white, hard, and brittle, and sometimes by its presence, confers peculiar characters on steel. A little iron in manganese renders it magnetic, and diminishes its tendency to oxidizement.





CHARACTERS OF THE SALTS OF IRON. The salts of iron are mostly soluble in water, and the solution is reddish brown, or becomes so by exposure to air. They afford either a pale or a deep blue precipitate with ferrocyanuret of potassium; and a black precipitate with hydrosulphuret of ammonia. The protosalts, when *entirely* free from peroxide, give a white precipitate with ferrocyanuret of potassium; the sesquiferrocyanuret of potassium precipitates them deep blue, but occasions no precipitate in pure solutions of peroxide. Infusion of gall-nuts produces a black or deep-purple precipitate. Hydriodic acid occasions no change. Soda-muriate of gold is an extremely delicate test of the protosalts of iron. A grain of protosulphate of iron, with an equal weight of soda, dissolved in four pints of water, produces a precipitate, gradually becoming purple, on the addition of a drop of solution of muriate of gold: without the soda, the effect did not appear in less than three days. (Ficinus, *Quart. Journ.*, xv. 382.)

Some of the persalts of iron, and especially the permuriate and the persulphate, are rendered of a peculiar blood-red colour, and furnish a red precipitate, when the solutions are concentrated, upon the addition of sulphocyanic acid and the soluble sulphocyanates: a very similar discoloration is effected by the meconic acid and the soluble meconiates, and by tinctures of opium. The effects may, to a certain extent, be distinguished by the addition of a few drops of muriate of gold, which destroys the tint occasioned by sulphocyanic compounds, but produces little effect upon those of the meconic acid. The indigotic acid also renders the persalts of iron of a red-colour. None of the metals precipitate iron in a metallic state, if we except zinc and cadmium, which effect an imperfect precipitation, especially from some of its protosalts, in vessels excluded from the access of air. Before the blowpipe, peroxide of iron produces with microcosmic salt, or borax, in the exterior flame, a glass, which is blood-red while hot, but yellow when cold. The protoxide forms with these fluxes a green glass, which, by increasing the proportion of the metal, passes through bottle-green to black, and is opaque. The glass from the peroxide becomes green in the interior flame, and is reduced to protoxide, and becomes attractable by the magnet. When placed on the wick of a candle, it burns with the crackling noise peculiar to iron.

MANUFACTURE OF IRON AND STEEL. It has already been stated that the nodular argillaceous carbonated iron-ore of the coal formation, is chiefly resorted to in this country as the source of the metal; the following is an outline of the process of reduction, (*Aikins' Dictionary: Supplement to the Encyclopædia Britannica: Lardner's Cyclopædia.*)

The first process that the ore undergoes after it has been broken into small pieces, is *roasting*. This is performed as follows:— Upon an oblong piece of firm and level ground is laid a bed of small coal, from four to eight inches thick; upon this is placed a stratum of ironstone, from eighteen inches to two feet thick: the upper surface of which is rendered more compact by filling up the interstices with smaller pieces. Upon this rests a layer of small coal not more than two inches thick, and on this, as a base, is reared a gradually-diminishing pile of ore; finally, the whole external surface receives a complete covering of small coal and coal-dust. The pile is kindled by applying burning coals to the lower

stratum. The breadth of the pile at the bottom varies from ten to sixteen feet, the usual height is about five feet, and the length varies from thirty feet to sixty yards. When the coals are consumed, the pile gradually cools, and in eight or ten days may be wheeled away to the furnace. The ore, if well roasted, will now be of a reddish brown colour, of diminished specific gravity, and will have become magnetical; the sulphur, water, inflammable matter, and carbonic acid that it originally contained, will have been dissipated, and it is now ready to be *smelted*. The *smelting-furnace* resembles externally a truncated quadrilateral pyramid of considerable height in proportion to its thickness; it is built of strong masonry, with contrivances to obviate the danger of its cracking by the expansion that takes place when it is heated. The interior of the furnace consists of the five following parts, reckoning from the bottom upwards. The *hearth*, composed of a single block of quartz-grit about two feet square: upon this is erected what in France and Germany is called the *crucible*, which is a four-sided cavity six feet six inches high, slightly enlarging upwards so as to be two feet six inches square at the top: the part above, called the *boshes*, is in the shape of a funnel or inverted cone, eight feet in perpendicular height, and twelve feet in diameter at the top; this terminates in the *cavity* of the furnace, which is of a conical figure, thirty feet high, and three feet diameter at the top; from this part it enlarges into a funnel-shaped *chimney*, about eight feet high, and sixteen in diameter at its mouth. About two feet above the hearth is a round aperture, called the *Tuyere*, or *Tweer*, made in one of the sides of the crucible to admit the extremity of the blast-pipe, through which the air in a high state of compression is forced into the furnace, and at the bottom of the crucible is an aperture, through which the scoriæ and melted metal are from time to time discharged. A furnace of this construction, if it meets with no accident, may be kept in constant work for three years or more without requiring any repairs. The furnace is charged at the chimney, by regular intervals, with coke, iron-ore, and limestone, in the proportion of about four of the first, three and one-third of the second, and one of the third, by weight, care being taken so to regulate the frequency of the charges, as that the furnace shall be always full nearly to the top of the great cavity. The density of the blast and the form of the discharging-pipe are ordered so that the chief focus of heat is about the bottom of the boshes; hence the ore has to descend about thirty-eight feet perpendicular, before it arrives at the place where the fusion is effected. This does not happen in less than forty-eight hours; so that the ore is all this time in a state of cementation at a high temperature, in contact with the burning fuel, and, in consequence, is almost saturated with carbon when it reaches the hottest part of the furnace. Being arrived at this place, the limestone flux, and the earthy particles of the coke and ore, run down into a slag\*; the iron is also melted,

\* The *slag* chiefly consists of silica in combination with lime, alumina, magnesia and the protoxides of manganese and iron. According to Mitscherlich, (*Ann. de Chim et Phys.*, xxiv,) it frequently consists of a bisilicate of lime and magnesia with more or less protoxide of iron: and this compound even forms crystals resembling *pyroxene*. The production of *artificial minerals* by these processes, is a subject of extreme interest and importance, both in a geological and chemical view, and an excellent field for experimental inquiry.

and more or less decarbonized, and in part oxydated by the blast, inversely, according to the proportion of fuel with which it is mixed. The fluid mass soon sinks down below the influence of the blast, and while it remains quiet at the bottom of the furnace, the globules of iron are precipitated from the slag, and occupy the lowest place, while the covering of scoriæ thus interposed between the metal and that portion of the blast which is reflected downwards, prevents it from suffering any further loss of carbon. In proportion as the melted matter accumulates, the slag being the uppermost, flows out at the aperture made for this purpose: the iron is let out at regular intervals, into furrows made in sand, where it forms what is called *pig-iron*, or into a large reservoir, whence it is poured by means of ladles into moulds, forming all the various articles of *cast-iron* ware.

The following are some of the circumstances in the smelting which influence the quality of the produce. Much depends on the *fuel*: if the coke is not perfectly made, but retains bitumen, the whole mass cakes in the upper part of the furnace, and, instead of descending regularly to the focus of heat, falls down at irregular intervals, so that part of the metal is detained too long before the blast, and decarbonized and oxydated, while other portions pass so rapidly through the furnace as never to be thoroughly reduced; hence the amount of the produce is diminished, and its quality deteriorated. Nor is it of less importance that the coke should be dry when put into the furnace. The *proportion of fuel* should also be adapted to the richness of the ore, so that there may be sufficient both to keep up the necessary degree of heat, as well as to carbonize the metal: hence, as the charges of ore and fuel are always proportioned by measure, if an ore somewhat richer than usual happens accidentally to be employed without a corresponding addition of fuel, the produce, though somewhat increased in quantity, will be more than equivalently reduced in quality. Another circumstance that the manufacturer must carefully attend to, is the proper choice of ore with regard to *fusibility*; for, as it is not only requisite that the iron should be melted, but also highly carbonized, and as coke gives off its carbon more difficultly than charcoal, a very fusible ore would melt long before it arrived at the focus of the furnace, and passing rapidly through, would reach the hearth without having had time to imbibe the proper quantity of carbon. Hence it is, that the rich *hæmatites*, although they afford an excellent quality of iron when smelted with charcoal, produce nothing but white iron when treated in the coke-furnace; while, on the other hand, *argillaceous ironstone* being much more refractory, does not melt till it comes into the very hottest part of the furnace, and therefore has had full time to absorb the desirable quantity of carbon. Another thing to be attended to, is the *proper regulation of the blast*, and this depends upon its dryness, its temperature, its compression, and its direction. The dryness and temperature appear to be principally governed by the season of the year. The drier and colder the air is, the greater will be its effect on the combustion; and it is found that the produce of iron during the summer months, is inferior in quantity and quality to that which is manufactured in the winter; a clear, dry, and severe frost is the most favourable period in every respect for the working of the furnace, and a change to snow or rain is followed by a

corresponding deterioration. The higher the temperature of the blast when it is delivered into the furnace, the smaller will be the quantity of oxygen contained in every cubic foot, and, of course, the vigour of the combustion\*. Nor is the force of the blast and its direction a subject of less importance; it is obvious, that in proportion as the charge descends, the carbonaceous matter is continually diminishing; hence the proper situation for the focus of the blast is that part of the furnace, where, when the ore shall have arrived, it will be fully carbonized and surrounded with a sufficient quantity of fuel to excite an intense heat, and absorb nearly the whole of the oxygen of the air, and thus prevent it from either oxydating the iron, or carrying off the carbon with which it may be combined. This precise situation, in a furnace properly constructed, will be found to be just within the expansion of the boshes; but as this is more than four feet above the tuyere hole, the blast must be delivered with great velocity, and in a direction somewhat slanting upwards, in order that it may be reflected by the opposite wall of the crucible, and arrive

\* Since this excellent account of the manufacture of iron (by Messrs. Aikin) was written, an important change has been suggested in the introduction of the blast, in consequence of the discovery by Mr. Neilson, of Glasgow, of the saving of fuel and improvement in the iron, by sending a blast of *hot*, instead of cold, air, into the furnace. A short notice of this discovery is given by Dr. Clark, in the *Edin. Phil. Trans.*, vol. xiii., of which the following is an abstract. The improvement consists essentially, in *heating* the air in its passage from the blowing-machines to the furnace, and the following are the results of this system, obtained in the Clyde Iron-Works.

During the first six months of the year 1829, when all the cast-iron in the Clyde Iron-Works was made by means of the cold blast, a single ton of cast-iron required for fuel to reduce it, 8 tons  $1\frac{1}{4}$  cwt. of coal, converted into coke. During the first six months of the following year, when the air was heated to near  $300^{\circ}$  Fahr., one ton of cast-iron required 5 tons  $3\frac{1}{4}$  cwt. of coal, converted into coke. The saving amounts to 2 tons 18 cwt. on the making of one ton of cast-iron; but from that saving comes to be deducted the coals used in heating the air, which were nearly 8 cwt. The net saving thus was  $2\frac{1}{2}$  tons of coal on a single ton of cast-iron. But during that year, 1830, the air was heated no higher than  $300^{\circ}$  Fahr. The great success, however, of those trials, encouraged the iron-masters to try the effect of a still higher temperature. Nor were their expectations disappointed. The saving of coal was

greatly increased, insomuch that, about the beginning of 1831, Mr. Dixon, of Calder Iron-Works, attempted the substitution of raw coal for coke. The attempt was entirely successful; and, since that period, the raw coal has been adopted in the majority of the Scotch iron-works. The temperature of the air under blast had now been raised so as to melt lead, and sometimes zinc, and therefore was above  $600^{\circ}$  Fahr., instead of being only  $300^{\circ}$ , as in the year 1830. It became, in consequence, so much elevated in temperature as to require the adoption of an old invention called the *water-tweer*, which consists in surrounding the tuyere with water. The water is kept continually changing as it heats, by means of one pipe to admit the water cold, and another to let it escape when heated.

During the first six months of the year 1833, when all these changes had been fully brought into operation, one ton of cast-iron was made by means of 2 tons  $5\frac{1}{4}$  cwt. of *coal*, (not previously converted into coke.) Adding to this, 8 cwt. of coal for heating, we have 2 tons  $13\frac{1}{4}$  cwt. of coal required to make a ton of iron; whereas, in 1829, when the cold blast was in operation, 8 tons  $1\frac{1}{4}$  cwt. of coal had to be used. This being almost exactly three times as much, we have, from the change of the cold blast to the hot, combined with the use of coal instead of coke, *three times as much iron made from any given weight of splint coal*. The efficacy of a given quantity of air, in the production of iron, is also greatly increased, and the requisite proportion of flux diminished.

at its proper place without undergoing any material decomposition. When the blast enters too rapidly, and in too concentrated a state, it renders the line of its passage, before it is reflected, so cool, that the descending slag which comes within its influence is suddenly solidified, and blown into a tube, reaching, perhaps, half-way across the crucible, through which the blast continues to rush; and in consequence of this protection, is conveyed with greater precision, and in a less decomposed state, into the upper part of the furnace. If, after this, the compression of the air is somewhat diminished, the tube still remains firm, often for days together, and the furnace works in the best manner. But, on the other hand, when too loose and soft a blast is admitted, and more especially if it is charged with moisture, it is unable to reach the top of the crucible without being decomposed, and the reflection which it undergoes from the wall of the crucible, weakens and disperses it to such a degree, that the combustion which ought to take place within the boshes, now occupies the whole

In regard to the *cause* of the above results, Dr. Clark observes, that it is necessary to discriminate between the quantity of fuel consumed, and the temperature produced. For instance, we may conceive a stove at the temperature of  $590^{\circ}$ , and lead put into it to melt. Then, since the melting-point of lead is more than  $100^{\circ}$  higher, it is evident that whatever fuel might be consumed in keeping that stove at  $500^{\circ}$ , is consumed to no purpose. In the manufacture of cast-iron likewise, a certain temperature is required to work the furnace favourably, and all the fuel consumed to produce any *lower* degree of temperature, is consumed in vain. How the hot blast serves to increase the *temperature* of a furnace, will appear on adverting to the relative weights of the solid and of the gaseous materials made use of in the reduction of iron. As nearly as may be, a furnace, as wrought at Clyde Iron-works, had two tons of solid materials an hour put in at the top, and this supply was continued for 23 hours a-day; one half-hour every morning, and another every evening, being consumed in letting off the iron. But the gaseous material—the hot air—what might be the weight of it? This can easily be ascertained thus: I find, by comparing the quantities of air consumed at Clyde Iron-works, and at Calder Iron-works, that one furnace requires of hot air from 2500 to 3000 cubical feet in a minute. I shall here assume 2867 cubical feet to be the quantity; a number that I adopt for the sake of simplicity, inasmuch as, calculated at an avoirdupois ounce and a quarter, which is the weight of a cubical

foot of air at  $50^{\circ}$  Fahr., these feet correspond precisely with 2 cwt. of air a minute, or *six tons an hour*. Two tons of solid material an hour, put in at the top of the furnace, can scarce hurtfully affect the temperature of the furnace, at least in the hottest part of it, which must be far down, and where the iron, besides being reduced to the state of metal, is melted, and the slag too produced. When the fuel put in at the top is coal, I have no doubt that, before it comes to this far-down part of the furnace—the place of its useful activity—the coal has been entirely coked; so that, in regard to the fuel, the new process differs from the old much more in appearance than in essence and reality. But if two tons of solid material an hour, put in at the top, are not likely to affect the temperature of the hottest part of the furnace, can we say the same of six tons of air an hour, forced in at the bottom near that hottest part? The air supplied is intended, no doubt, and answers to support the combustion; but this beneficial effect is, in the case of the cold blast, incidentally counteracted by the cooling power of six tons of air an hour, or two cwt. a minute, which, when forced in at the ordinary temperature of the air, cannot be conceived otherwise than as a prodigious refrigeratory passing through the hottest part of the furnace, and repressing its temperature. The expedient of previously heating the blast obviously removes this refrigeratory, leaving the air to act in promoting combustion, without robbing the combustion of any portion of the heat it produces. (See Dr. Clark's paper.)

upper part of the crucible: in consequence of this, the tube of scoriæ is presently burnt away, the iron, almost as fast as it is melted, is ignited and oxidized, the tuyere-hole glows, like the sun, with an intensely vivid white light; the scoriæ, from being yellowish-white streaked with blue, become green, brown, and finally black, nearly the whole of the iron in the state of oxide being taken up by it; the blocks of refractory grit-stone, with which the lower part of the furnace is lined, are worn into great holes, and in the space of a few hours prodigious damage is sustained. (Aikin's *Dictionary*, Art. IRON.)

VARIETIES OF IRON. An extremely important part of the chemical history of iron relates to the varieties of the metal which are found in commerce. These are much too numerous to be dwelt upon here; so that we shall limit our observations to the principal of them only, which are *cast-iron*, *wrought-iron*, and *steel*.

*Cast-iron* is essentially a *subcarburet*. There are two principal varieties of it, distinguished by the terms *white* and *gray*. *White cast-iron* is very hard and brittle, and, when broken, of a radiated texture. Acids act upon it but slowly, and exhibit a texture composed of a congeries of plates, aggregated in various positions. (Daniell, *Quarterly Journal of Science and Arts*, vol. ii., p. 280.) *Gray or mottled-iron* is softer and less brittle; it may be bored and turned in the lathe. When immersed in dilute muriatic acid, it affords a large quantity of black insoluble matter, which Mr. Daniell considers as a triple compound of carbon, iron, and silicium, and which has some very singular properties. The texture of the metal resembles bundles of minute needles. This variety of iron is occasionally substituted for wrought-iron, from its toughness, and comparative purity: it sometimes contains only 3 to 4 *per cent.* of foreign matter. Beams, employed in building, and various parts of machinery which formerly were exclusively made of wrought-iron, are now cast. A curious operation is often performed upon small articles made of cast-iron, in order to convert them into malleable iron, which is termed *decarbonization*, and is sometimes practised upon steel; it consists in bedding the articles in powdered oxide of iron (*hæmatite* is generally used), and exposing them to a red-heat: the carbon is thus abstracted from the cast-iron, and it becomes as flexible and malleable as wrought-iron.

*Wrought-iron*. Cast-iron, after it has been, to a certain extent, *refined*, by fusion in a forge, in contact with charcoal, is in this country converted into wrought-iron by a curious process, called *puddling*. The cast-iron is put into a reverberatory furnace, and when in fusion is stirred, so that every part may be exposed to the air and flame. After a time the mass heaves, emits a blue flame, and gradually grows tough, and becomes less fusible, and at length pulverulent; the fire is then urged, so that the particles again agglutinate at a welding-heat, and are gradually wrought up into masses. In that state of intense heat the masses are passed successively between rollers, by which a large quantity of extraneous matter is squeezed out, and the iron becomes malleable. The bars, into which it is formed, are cut into pieces, placed in parcels in a very hot reverberatory, and again hammered, or rolled out into bars. They are thus rendered more tough, flexible, and malleable, but much less fusible, and may be considered as nearly *pure iron*.

Analysis shows that cast-iron contains carbon, often sulphur, phosphorus, manganese, and silicium; and it appears probable that calcium exists in some of the varieties. A specimen of good cast-iron, analyzed by Berzelius, afforded iron 91.53—manganese 4.57—carbon 3.90. By the processes of puddling and rolling, the principal part of the foreign substances are burned away or squeezed out, and thus malleability is conferred upon the metal by rendering it more pure. A bar of wrought-iron, when its texture is examined in the mode pointed out by Mr. Daniell, presents a fasciculated appearance, the fibres running in a parallel and unbroken course throughout its length. This structure may be well seen by tearing a bar of wrought-iron asunder.

**MANUFACTURE OF STEEL.** This extraordinary and valuable substance is a compound of iron with a small relative proportion of carbon\*, which varies in the varieties of steel. Other substances are also occasionally present, which apparently modify some of its characters: traces of phosphorus, sulphur, and manganese, are not uncommon. It combines the fusibility of cast with the malleability of bar-iron, and when heated and suddenly cooled it becomes very *hard*, but may again be softened by the careful management of heat; hence its superiority for the manufacture of cutting-instruments, and an almost infinite number of useful purposes in the arts. If kept for a long time in fusion it loses carbon, and becomes pure iron. Its texture, when examined by the action of an acid, is not fibrous, but lamellated.

Iron is converted into steel by a process called *cementation*, which consists in heating bars of the *purest* iron in contact with charcoal: it absorbs carbon and increases in weight†, at the same time acquiring a *blistered* surface. This, when drawn down into smaller bars and beaten,

\* The identity of charcoal and diamond above adverted to, receives additional proof by the conversion of iron into steel when that metal is ignited with diamond powder. Upon this subject some controversy will be found in the *Phil. Mag.*, vol. v.; the *experimentum crucis* is, however, due to Mr. Pepys, who availed himself of Mr. Children's Voltaic battery of large plates for the production of the requisite heat (*Phil. Trans.*, 1815, p. 371): he bent a wire of pure soft iron so as to form an angle in the middle, in which part he divided it longitudinally by a fine saw; in the opening so formed he placed diamond-powder, securing it in its situation by two finer wires, laid above and below it, and kept from shifting by another small wire, bound firmly and closely round them. All the wires were of pure soft iron, and the part containing the diamond-powder was enveloped by thin leaves of talc. Thus arranged, the apparatus was placed in the electrical circuit, where it was kept red-hot for six minutes: on opening the wire the diamond had disappeared, the interior sur-

face of the iron had fused into numerous cavities, notwithstanding the very moderate heat to which it had been exposed, and all that part which had been in contact with the diamond was converted into perfect blistered-steel. A portion of it being heated red and plunged into water, became so hard as to resist the file and to scratch glass.

† The following table, drawn up by Mr. Mushet, shows the quantities of charcoal which disappeared during the conversion of iron into the different *subcarburets of iron* known in commerce. (*Phil. Mag.*, xiii.)

Charcoal absorbed.	RESULTS.
$\frac{1}{20}$	soft cast-steel.
$\frac{1}{10}$	common cast steel.
$\frac{1}{5}$	the same, but harder.
$\frac{1}{3}$	the same: too hard for drawing.
$\frac{1}{2}$	white cast-iron. [ing.
$\frac{1}{1}$	mottled cast-iron.
$\frac{1}{1}$	black cast-iron.

When the carbon amounts to  $\frac{1}{60}$  of the whole mass, the hardness is at a maximum.

forms *tilted-steel*; and this broken up, heated, welded, and again drawn out into bars, forms *shear-steel*. *English cast-steel* is prepared by fusing blistered-steel with a flux composed of carbonaceous and vitrifiable ingredients, casting it into ingots, and afterwards, by gentle heating and careful hammering, or rolling, giving it the form of bars.

WOOTZ, OR INDIAN STEEL, which has, by some, been considered as superior to any other, for the purpose of making certain edge-tools, apparently derives its peculiar excellence from combination with a minute portion of aluminum and silicium. (*Quart. Jour. of Science*, vii., 288.) Whether these substances are in the ore, or are furnished by the crucible used in making the steel, is not certainly known. Wootz, in the state in which it is imported, is not fit to make into fine cutlery; it requires a second fusion, by which the whole mass is purified and equalized, and fitted for forming the finest edge-instruments.

CASE-HARDENING is an operation performed upon cast or wrought-iron, by which it is superficially converted into steel: the article is for this purpose either heated to redness in a crucible, or vessel containing charcoal powder; or sometimes, if small and delicate, is wrapped round with leather, and then gradually heated to redness, and kept in that state till its surface is duly carbonized.

HARDENING AND TEMPERING STEEL. When steel is heated to a cherry-red colour, and then plunged into cold water, it becomes so extremely hard and brittle, as to be unfit for almost any practical purpose. To reduce it from its extreme hardness, is called by the workmen *tempering*, and is effected by again heating the steel to a certain point. The surface being a little brightened, exhibits, when heated, various colours, depending upon the formation of thin films of oxide\*, which constantly change as the temperature is increased, and by these colours it has been customary to judge of the temper of the steel. But a more accurate, as well as convenient method, is to use a bath and thermometer; the bath may be of mercury, or of the fusible mixture of lead, tin, and bismuth, or, indeed, of any fluid whose boiling-point is not much under 600°. Into this bath the articles to be tempered are put, together with the bulb of a thermometer graduated to near the boiling-point of mercury. The corresponding *degrees* at which the various colours appear are from 430° to 600°. The first change is at about 430°, but this is too faint to be distinguished, except by comparison with another piece of untempered polished steel. At 460° the colour is *straw*, becoming deeper as the temperature is increased; at 500° the colour is *brown*; this is followed by a *red* tinge with streaks of *purple*, then *purple*, and at nearly 600° it is *blue*. The *degrees* at which the respective colours are produced being thus known, it follows that the workman has only to heat the bath, with its contents, up to the required point. For example, suppose the blade of a penknife (or one hundred of them) to require tempering: they are suffered to remain in the bath until the mercury in the thermometer rises to 460°, and no longer, that being the heat at which the knife (supposing

\* That the colour produced on the surface of heated steel is the effect of oxidation, is proved from the circumstance that when steel is heated and suffered to cool under mercury or oil, none of the colours appear; nor do they when it is heated in hydrogen or nitrogen.



it to be made of the best English cast-steel) will be sufficiently tempered. The advantages attending this method are obvious: the heat is equally applied to the whole; and the workman, instead of attending to the colour of each blade, has only to observe the thermometer.

Some recent experiments, proving that steel, for certain uses, is sufficiently tempered long before it is heated to produce any change of colour, promise to give additional value to this process by a thermometer. The knife-edges attached to the pendulum described by Capt. Kater, (*Phil. Trans.*, 1818, p. 38,) were forged by Mr. Stodart, from a piece of fine wootz. They were carefully hardened, and tempered in the bath at  $430^{\circ}$ ; on trial they were found too soft. They were a second time hardened, and then heated to  $212^{\circ}$ . The intention was to increase the heat from that point, trying the temper at the advance of about every ten degrees. In the present instance this was not necessary, the heat of boiling water proving to be the exact point at which the knife-edges were admirably tempered. It is highly probable that steel, for many uses, may be sufficiently tempered in a range so extensive as from  $212^{\circ}$  to  $430^{\circ}$ , and, by the thermometer, all the intervening degrees may be certainly ascertained.

The quality of steel is sometimes tested by washing over its clean surface with dilute nitric acid, which ought to produce an uniform gray or blackish colour: if the steel is imperfect, and contains veins or pins of iron, they become evident by their difference of colour. When some particular kinds of iron or steel are thus tested, a mottled appearance is produced, as if it were composed of layers or wires of iron and steel welded together: hence is supposed to arise the peculiar character of the celebrated *Damascus* sword-blades.

ALLOYS OF STEEL. Attempts have been made to improve the quality of steel by alloying it with some other metals, but none of these combinations have been found, after due experience, to be superior to the best ordinary steel. We shall again have occasion to notice them; but for details upon this subject, the reader is referred to the papers of Messrs. Stodart and Faraday, already quoted (*Quart. Jour.*, ix., 319), and to the volume of Dr. Lardner's *Cyclopædia*, treating on iron and steel.

## § X. ZINC.

ZINC is found in the state of oxide and of sulphuret. The metal zinc is first mentioned by Paracelsus, but the use of its ores, in converting copper into brass, was probably known to the ancients. Perfectly-pure zinc is very difficultly obtained; it may be procured in a state approaching to extreme purity, by dissolving the purest kinds of zinc that occur in commerce in dilute sulphuric acid, and immersing a plate of zinc for some hours in the solution, which is then filtered, decomposed by carbonate of potassa, and the precipitate, after having been welledulcorated, heated with charcoal in an iron or earthen retort in a proper furnace. The zinc being volatile at a white-heat may thus be distilled over into water, care being taken that the neck of the retort is short and wide, otherwise it will be stopped up by the condensed metal. The common zinc of commerce generally contains a portion of lead, copper, iron, traces of arsenic

and manganese, and a little plumbago: these impurities chiefly remain in the form of a black powder when it is dissolved in dilute sulphuric acid.

Zinc is a blueish-white metal, with considerable lustre, of a specific gravity of about 6.8 in its usual state; but, when drawn into wire, or rolled into plates, its density is augmented to 7 or 7.2. In its ordinary state, at common temperatures, zinc is tough, and with difficulty broken by blows of the hammer. It becomes very brittle when its temperature approaches that of fusion, which is about  $773^{\circ}$ ; but at a temperature a little above  $212^{\circ}$ , and between that and  $300^{\circ}$ , it becomes ductile and malleable, and may be rolled into thin leaves, and drawn into moderately fine wire, which, however, possesses but little tenacity. When a mass of zinc, which has been fused, is slowly cooled, its fracture exhibits a lamellar and crystalline texture. The equivalent of zinc is 32. (32.2 Gmelin; 32.3 Turner.)

When a surface of clean zinc is exposed to air and moisture at common temperatures, it soon tarnishes, and acquires a dull-gray colour from superficial oxidizement: it then remains for a long time unchanged. It has lately, in consequence of its lightness and cheapness, been much used for roofing, gutters, and chimney-tops: but it should not, as is generally the case, be rivetted with copper nails, the contact of which with the zinc will probably accelerate the decay of the latter by electric action.

**ZINC AND OXYGEN.** The high attraction which subsists between zinc and oxygen, is shown by the facility with which nearly all the other metallic oxides, when in solution, are reduced to the metallic state by its means. Its important electro-generative power, in the Voltaic apparatus, is also referable to this cause. When-zinc filings are put into water, and air carefully excluded, they suffer little change; but if air be admitted, hydrogen is gradually evolved, and the metal becomes incrustated with a gray powder. The same product is obtained by long exposure of zinc to moist air, or by exposing the metal to the joint action of heat and air at a temperature just sufficient to fuse it. This is probably a mere mixture of metallic zinc and oxide of zinc; by some it is regarded as a true *sub-oxide*, and a similar compound is obtained, according to Dulong, by decomposing oxalate of zinc at a red-heat in a retort.

**PROTOXIDE OF ZINC.** ( $Zn + O$ ) or  $Zn$ . This is the only salifiable oxide of zinc: it is obtained by intensely heating the metal exposed to air. At a high red-heat it takes fire, and air being freely admitted, burns with a very bright flame, and is converted into a white flocculent tasteless substance, formerly called *nihil album*, *philosopher's wool*, and *flowers of zinc*. As prepared by combustion it contains small particles of the metal, which always render it gritty, and require to be separated by washing; hence, for pharmaceutical use, it is best prepared by precipitating solution of sulphate of zinc by ammonia, and washing and drying the precipitate. It has been used as a pigment, both with oil and water; and is employed in medicine as a tonic, and as an external application. It is sometimes made upon a large scale, and is then seldom pure, being tainted by oxide of iron and other substances: the whiter parts of such oxide used to be called *pompholix*, and the gray, or less pure portions, *tutty*. If it be removed in large flakes from the crucible in which it is forming, and

carried into a dark room, they continue for some time luminous. This oxide, when pure, is perfectly white; at a high temperature it acquires a tint of yellow, but again whitens as it cools. It is readily soluble in the acids; it also dissolves in the caustic fixed alkalis, and in pure and carbonated ammonia. The strong ammoniacal solution becomes turbid when diluted, and deposits its oxide when boiled. The solutions in potassa and soda yield a white deliquescent mass on evaporation: these, however, can scarcely be called chemical combinations. When a solution of alumina in caustic potassa is mixed with an ammoniacal solution of oxide of zinc, a definite combination of the earth and oxide is thrown down, containing, according to Berzelius, 6 proportionals of alumina and 1 of oxide of zinc, and being identical in composition with the mineral called *Gahnite*. The solutions of zinc decomposed by the alkalis furnish bulky white precipitates, consisting of *hydrated oxide*; this loses water at a red-heat, and is then of the same composition as the oxide obtained by the rapid combustion of the metal. Thenard has described a *peroxide of zinc* obtained by agitating the hydrated oxide with oxygenated water: at all events this is no permanent compound, and certainly forms no distinct salts with the acids; we may, therefore, reject the suboxide and the peroxide of zinc, as indefinite compounds, and consider this metal as susceptible of one degree of oxidizement only, forming the protoxide, composed of

						Proust.	Berzelius.	Döbereiner.		
Zinc	..	1	..	32	..	80	..	80.1	..	81.64
Oxygen	..	1	..	8	..	20	..	19.9	..	18.36
		1		40		100		100.0		100.00

CHLORIDE OF ZINC ( $Zn + Cl$ ) is formed by heating leaf-zinc in chlorine, or by evaporating a solution of zinc in muriatic acid to dryness, and heating the residue red-hot in a glass tube. It is also obtained by distilling a mixture of zinc-filings and corrosive sublimate, or a mixture of dried sulphate of zinc and chloride of sodium. It is a white semitransparent substance, fusible at about  $212^{\circ}$ , and volatile at a red-heat. It was formerly called *butter of zinc*. It is readily soluble in water, and the solution gives on evaporation a very difficultly crystallizable and extremely deliquescent salt, generally called *muriate of zinc*, and which, when heated in the open air, partly sublimes in the form of chloride, and is partly resolved into muriatic acid and oxide of zinc in consequence of the presence of water. Its concentrated solution deposits oxide of zinc upon the addition of water, and the diluted solution dissolves the oxide when concentrated by evaporation. The solution of muriate of zinc is always slightly acid, and the addition of ammonia does not render it neutral till all the oxide is precipitated. The attraction of zinc for chlorine is so great, that it is often employed for separating chlorine from other combinations.

Chloride of zinc consists of

						J. Davy		
Zinc	. .	1	..	32	..	47	..	50
Chlorine	. .	1	..	36	..	53	..	50
		1		68		100		100

CHLORATE OF ZINC ( $Zn + Cl'$ ) crystallizes in octoëdra, and is a very soluble salt. It is best obtained by dissolving carbonate of zinc in chloric acid. When metallic zinc is digested in chloric acid, a portion of chloride of zinc is formed.

IODIDE OF ZINC. ( $Zn + I$ ) Iodine and zinc readily combine, and produce a fusible, volatile, and crystalline compound, which, when exposed to air, deliquesces into *hydriodate of zinc*. Heated in contact of air, it is resolved into iodine and oxide of zinc. It consists of

							Gay Lussac.
Zinc . . .	1	. . .	32	. . .	20.4	. . .	20.48
Iodine . . .	1	. . .	125	. . .	79.6	. . .	79.52
	1		157		100.0		100.00

IODATE OF ZINC. When iodate of potassa is added to solution of sulphate of zinc, it forms a very difficultly-soluble iodate of zinc.

BROMIDE OF ZINC. The action of bromine and of bromic acid upon zinc has not been particularly examined.

FLUORIDE OF ZINC is very difficultly soluble: with fluoride of potassium it forms a more soluble triple salt.

NITRATE OF ZINC is a deliquescent salt, which crystallizes with difficulty in four-sided prisms. They are copiously soluble in water and alcohol, and consist of one proportional of acid, one of oxide, and six of water.

SULPHURET OF ZINC ( $Zn + S$ ) exists native under the name of *Blende*. It may be formed artificially by heating oxide of zinc with excess of sulphur, and is then of a yellow-brown colour. It is also produced by heating rapidly and suddenly a mixture of zinc-filings and sulphuret of mercury: the mercury is revived, and intense action ensues during the union of the zinc and sulphur. By passing the vapour of sulphur over fused zinc, Mr. E. Davy obtained a white crystalline substance resembling native phosphorescent blende. Sulphuret of zinc consists of

							Arfwedson.
Zinc . . .	1	. . .	32	. . .	66.5	. . .	66.34
Sulphur . . .	1	. . .	16	. . .	33.5	. . .	33.66
	1		48		100.0		100.00

When a salt of zinc is precipitated by hydrosulphuret of potassa, a white compound is obtained, composed, according to Berzelius, of 72 oxide of zinc, 25 sulphuretted hydrogen, 3 water.

*Native Sulphuret of Zinc.* *Blende* is a brittle soft mineral, of different shades of brown and black. Its primitive form is the rhomboidal dodecaëdron. It usually contains traces of iron and lead. It is an abundant mineral, and important as a source of the pure metal, which is obtained by roasting the ore, and afterwards exposing it to heat in proper distillatory vessels, mixed with charcoal. The English miners call it *black jack*.

HYPOSULPHITE OF ZINC ( $Zn + \underline{S}$ ) was obtained long ago by Fourcroy, who considered it as a *sulphuretted sulphite*. He formed it by digesting metallic zinc in sulphurous acid, sulphuretted hydrogen is disengaged, and by gentle evaporation crystals are obtained, which are to be digested

in alcohol; this liquid dissolves the hyposulphite, and affords it in prismatic crystals. A mixture of oxide of zinc and sulphur treated by sulphurous acid, affords the same salt; it is efflorescent, and easily decomposed by heat. (Fourcroy, *Système des Connoissances Chimiques*, v. 380.)

SULPHITE OF ZINC ( $ZN + \underline{S}$ ) is easily formed by dissolving the oxide in sulphurous acid; it is more easily crystallizable than the hyposulphite, and is insoluble in alcohol.

HYPOSULPHATE OF ZINC ( $ZN + \underline{S}'$ ) is obtained by adding a solution of hyposulphate of baryta to sulphate of zinc; it is very soluble, and difficultly crystallizable. The crystals are composed of

					Heeren.
Oxide of zinc . . . . .	1	..	40	..	24.2
Hyposulphuric acid . . . . .	1	..	72	..	43.4
Water . . . . .	6	..	54	..	32.4
	<hr/>		<hr/>		<hr/>
	1		166		100.0
					24.25
					43.51
					32.24
					<hr/>
					100.00

SULPHATE OF ZINC. ( $ZN + \underline{S}'$ ) Zinc is readily oxidized and dissolved by dilute sulphuric acid; hydrogen gas holding a little zinc in solution is given off, and a transparent colourless solution of *sulphate of zinc* results, which, by evaporation, affords crystals in the form of four-sided prisms, terminated by four-sided pyramids. They have been described by Mr. Brooke (*Ann. of Phil., N. S.*, vi., 437). It effloresces slightly in a dry air. It is soluble in 2.5 parts of water at 60°. It is prepared for the purposes of the arts from the native sulphuret, and is usually in the form of a white amorphous mass, called *white vitriol*, and is extremely impure. When heated, it fuses, and gradually gives out its water of crystallization; at a red-heat its acid begins to pass off, and at a very high temperature it is entirely decomposed, leaving oxide of zinc. It consists, in its anhydrous state, of

				Tennant.	Wenzel.
Oxide of Zinc . . . . .	1	..	40	..	50
Sulphuric acid . . . . .	1	..	40	..	50
	<hr/>		<hr/>		<hr/>
	1		80		100
					46.19
					53.81
					<hr/>
					100.00

The crystals are constituted of

					Mitscherlich.
Anhydrous sulphate of zinc . . . . .	1	..	80	..	56
Water . . . . .	7	..	63	..	44
	<hr/>		<hr/>		<hr/>
	1		143		100
					55.24
					44.76
					<hr/>
					100.00

TRIS-SULPHATE OF ZINC. ( $3ZN + \underline{S}'$ ). When oxide of zinc is boiled in a solution of sulphate of zinc, or when the salt is partially decomposed by potassa, and the precipitate which falls boiled in water, a salt is formed which crystallizes in opaque shining scales, composed according to Vogel, of 3 atoms of oxide of zinc and 1 of sulphuric acid.

AMMONIO-SULPHATE OF ZINC is obtained, according to Thomson, by mixing solutions of the two constituent salts in atomic proportions, and concentrating the solution. It crystallizes in white rhomboids, which readily dissolve in water, and consist of 1 equivalent of each of the sulphates, and 7 of water.

SULPHATE OF ZINC AND POTASSA forms flat rhomboidal crystals, per-

manent in the air, and soluble in 5 parts of water at 60°. (II. Stokes, *Phil. Mag.*, 2nd series, ii., 428.) They consist of 1 equivalent of each of the sulphates and 7 of water.

*Native Sulphate of Zinc* occurs at Holywell in Flintshire, and in other places where the sulphuret of zinc is found; it is probably the result of the decomposition of that ore, and is often found in the waters of the mines.

PHOSPHURET OF ZINC is a brilliant lead-coloured compound, formed by distilling in a coated retort a mixture of two parts of zinc, and one of phosphorus.

Neither *Hypophosphite* nor *Phosphite of Zinc* have been examined.

PHOSPHATE OF ZINC is not crystallizable. It may be obtained by dissolving zinc in phosphoric acid, and evaporating to dryness. A phosphate of zinc is also precipitated upon the addition of phosphate of soda to sulphate of zinc. These salts have not been precisely examined, but it is probable there is a *subphosphate*, a *phosphate*, and a *biphosphate* of zinc.

CARBONATE OF ZINC ( $Zn + CO_2$ ) may be formed by passing carbonic acid through water containing diffused hydrated oxide of zinc. The precipitate formed by adding carbonate of potassa to sulphate of zinc, is, according to Berzelius, a mixture of carbonate and hydrated oxide, analogous to the *magnesia alba*. Some of the varieties of *calamine* appear to consist of anhydrous carbonate of zinc. Specimens from Somersetshire and Derbyshire yielded

							Smithson.
Oxide of zinc	. .	1	..	40	..	64.5	.. 65
Carbonic acid	. .	1	..	22	..	35.5	.. 35
		1		62		100.0	100.

Another variety of *calamine*, from Bleiberg, in Carinthia, is probably a hydrous subcarbonate, consisting of

							Smithson.
Oxide of zinc	. .	3	..	120	..	71	.. 71.4
Carbonic acid	. .	1	..	22	..	13	.. 13.5
Water	. . . .	3	..	27	..	16	.. 15.1
		1		169		100	100.0

*Native Carbonate of Zinc; Calamine.* This mineral occurs both crystallized and massive; its primitive form is an obtuse rhomboid. It is often found investing carbonate of lime, which has sometimes been decomposed, and the *calamine* remains in pseudo-crystals. It abounds in Somersetshire, Flintshire, and Derbyshire. A beautiful variety, coloured by carbonate of copper, is found at Matlock. A variety of *calamine*, known by the name of *electric calamine*, from its property of becoming electrical when gently heated, consists of oxide of zinc in combination with silica.

REDUCTION OF THE ORES OF ZINC. The zinc of commerce is procured from the native sulphuret, and from *calamine*, by the following process. The ore is first picked and broken into small pieces, and then submitted to a dull red-heat in a reverberatory furnace, by which carbonic acid is driven off from the *calamine*, and sulphur from the

blende. It is then washed, ground, and thoroughly mixed with about one-eighth its weight of powdered charcoal. This mixture is put into large earthen pots, not unlike oil-jars, six of which are usually placed in a circular furnace; each pot has an iron tube passing from its lower part, through the floor of the furnace, and dipping into water; they are everywhere else firmly luted: upon the application of a red-heat, the metal distils through the tube into the water beneath, whence it is collected, melted, and cast into cakes.

BORATE OF ZINC is an insoluble white powder.

CYANURET OF ZINC forms an insoluble white powder, when solution of cyanuret of calcium is added to sulphate of zinc. By destructive distillation in a retort, it leaves a black *carburet of zinc*.

FERROCYANURET OF ZINC is thrown down in the form of a white gelatinous precipitate, when ferrocyanuret of potassium is dropped into solution of sulphate of zinc.

ZINCOCYANURET OF POTASSIUM. When cyanuret of zinc is dissolved in a solution of cyanuret of potassium, filtered, and evaporated, large octoëdral crystals are obtained, anhydrous, decrepitating when heated, and then fusing into a transparent colourless liquid. (L. Gmelin.)

ALLOYS OF ZINC. With *potassium* and *sodium*, zinc forms brittle alloys, decomposable by exposure to air and water. Its alloy with *manganese* is unknown. With *iron* it forms a white and somewhat malleable alloy, which is difficult to form; but if plates of hot-iron be dipped into melted zinc, they acquire the appearance of tin-plate.

CHARACTERS OF THE SALTS OF ZINC. They are mostly soluble in water, and the solutions are colourless and transparent, and have a peculiarly unpleasant metallic taste: they are not precipitated by hydriodic acid. Potassa, soda, and ammonia, form white precipitates, soluble in excess of the alkali, and in dilute sulphuric acid. Sulphuretted hydrogen throws down a white sulphuret of zinc in perfectly neutral solutions, but not in those which are acid or alkaline. Hydrosulphuret of ammonia produces a yellowish-white precipitate. The soluble phosphates, carbonates, and borates, produce white precipitates soluble in acids and alkalis. Infusion of galls occasions no precipitate. The salts which are insoluble in water dissolve in dilute sulphuric acid, and are precipitated by ammonia, but generally dissolve in excess of acid or of precipitant. Hydrosulphuret of ammonia precipitates the oxide of zinc. Metallic zinc is not thrown down from its solutions, by any of the other metals.

Before the blowpipe *oxide of zinc* becomes yellow when heated, but whitens as it cools. A small proportion forms with microcosmic salt and with borax a clear glass, which becomes opaque on increasing the quantity of oxide. A drop of nitrate of cobalt being added to the oxide, and dried and ignited, it becomes green. With soda, in the interior flame it is reduced, and burns with its characteristic flame, depositing its oxide upon the charcoal. By this process zinc may be easily detected even in the *automalite*. Mixed with oxide of copper, and reduced, the zinc will be fixed, and brass obtained. But one of the most unequivocal characters of the oxide of zinc is, to dissolve it in vinegar, evaporate the solution to dryness, and expose it to the flame of a lamp, when it burns with its peculiar flame.

## § XI. TIN.

TIN (Jupiter ♃ of the alchemists) has been known from the remotest ages. It was in common use in the time of Moses, and was obtained at a very early period from Spain and Britain by the Phœnicians. (PLINY, lib. iv., cap. 34, and xxxiv., cap. 47.) It occurs most abundantly in Cornwall; and is also found in Germany, Bohemia, and Hungary, in Europe; in Chili and Mexico; in the Peninsula of Malacca; and in the Island of Banca. A little tin has also been found at Fahlun and Utö, in Sweden. Several varieties of tin occur in commerce, respecting which Vauquelin has given an useful essay. (*Annales de Chimie*, lxxvii.) The *native oxide* is the principal *ore of tin*: the metal is obtained by heating it to redness with charcoal and a little lime. The common ores are known under the name of *mine-tin*, and furnish a less pure metal than that obtained from *stream-tin*. The former is usually called *block-tin*, the latter *grain-tin*. The processes of reduction are described at length in Aikin's *Dictionary* (Art. TIN); and by Mr. Taylor in the 5th volume of the *Geological Transactions*.

Tin has a silvery-white colour; it is malleable, though sparingly ductile. Specific gravity from 7.28 to 7.6, the lightest being the purest metal. When bent it occasions a peculiar crackling noise, arising from the destruction of cohesion among its particles, and hence the brittleness and want of tenacity of tin-wire. When rubbed it exhales a peculiar smell. It melts at 442°, and, by exposure to heat and air, is gradually converted into a white oxide. Placed upon ignited charcoal, under a current of oxygen gas, it enters into rapid combustion, forming the peroxide; and if an intensely-heated globule of the metal be thrown upon a sheet of paper, it subdivides into small particles, which burn very brilliantly. It volatilises at a very high temperature: when heated, its surface often becomes yellow and iridescent, in consequence of superficial oxidizement. The equivalent of tin is 58. (59, Gmelin; 57.9, Turner.)

A preparation, under the name of *powdered tin*, is sometimes directed to be made for pharmaceutical use, by shaking the melted metal in a wooden box rubbed with chalk on the inside: *tin-filings* have also a place in some *Pharmacopœiæ*, and have been used as a vermifuge. These preparations are, however, both dangerous, the metal being rendered poisonous in the former case by slight oxidation, (Orfila, *Traité des Poisons*, tom. i., 2me partie, p. 18,) and often creating very dangerous irritation when given in filings.

PROTOXIDE OF TIN (*sta + o*) is obtained by precipitating a solution of protochloride of tin by ammonia; it falls in the state of *hydrate*; when dried, out of the contact of air, it is of a gray colour, and undecomposable by heat. According to M. Cassola (*Ann. de Chim. et Phys.*, xiii., 40,) the protoxide is also obtained by pouring nitric acid diluted with ten times its volume of water upon tin filings, and leaving them in contact 48 hours. When protochloride of tin is decomposed by a carbonated alkali, and the precipitate carefully dried at a temperature below 212°, it is also a *hydrated protoxide*, retaining no trace of carbonic acid. The *anhydrous protoxide* is best obtained by heating the hydrate to redness, passing a current of dry carbonic acid over it till the water is carried off, and



suffering it to cool out of the contact of air. The specific gravity of this oxide is 6.6. It burns, on the contact of a red-hot wire, into peroxide. In the hydrated state it dissolves very readily in sulphuric, muriatic, and dilute nitric acids, and in caustic potassa and soda, but not in ammonia, nor in the alkaline carbonates. Its alkaline solution, when long kept, deposits metallic tin in arborescent crystals, and becomes a solution of the peroxide. Protoxide of tin consists of

						Berzelius.		Proust.		Gay Lussac.
Tin	. 1	.. 58	.. 87.8	.. 88.028	.. 87	.. 88.1				
Oxygen	1	.. 8	.. 12.2	.. 11.972	.. 13	.. 11.9				
	<u>1</u>	<u>66</u>	<u>100.0</u>	<u>100.000</u>	<u>100</u>	<u>100.0</u>				

SESQUIOXIDE OF TIN. ( $sta + 1\frac{1}{2}o$ .) When a saturated solution of peroxide of tin in muriatic acid is mixed with moist hydrated peroxide of iron, an interchange of elements takes place, by which chloride of iron and sesquioxide of tin are formed: its solubility in ammonia distinguishes it from protoxide; and its giving a purple precipitate with perchloride of gold, from peroxide.

PEROXIDE OF TIN ( $sta + 2o$ ) is formed by treating the metal with strong nitric acid: there is a violent action attended by the formation of nitrate of ammonia. Scarcely any of the metal is dissolved, but it remains as a yellowish powder, which may be purified by washing, and dried at a dull red-heat. It is also formed by projecting a sufficient quantity of nitre upon red-hot tin. Fused with glass, it forms *white enamel*; but alone, it is extremely infusible, and when it has been heated it is insoluble in acids. The substance called *Tin Putty*, is a peroxide of tin, formed by levigating the crusts of oxide that form upon the metal when kept for some time in fusion.

HYDRATED PEROXIDE OF TIN, formed by decomposing the solution of perchloride of tin by ammonia, is a bulky white precipitate, which, when dried at  $212^{\circ}$ , retains between 19 and 20 *per cent.* of water. In its moist state it dissolves in the acids, and in excess of ammonia and potash. When the white powder, obtained by the action of nitric acid on tin, is thoroughly edulcorated, it retains about 10 *per cent.* of water when dried in the air. The solutions of peroxide of tin in the acids are liable to spontaneous deposition of hydrated peroxide. As this oxide reddens litmus, and combines with bases, it has been termed *Stannic acid*. Peroxide of tin consists of

						John Davy.		Proust.		Gay Lussac.
Tin	. 1	.. 58	.. 78.4	.. 78.34	.. 78.4	.. 78.6				
Oxygen	2	.. 16	.. 21.6	.. 21.66	.. 21.6	.. 21.4				
	<u>1</u>	<u>74</u>	<u>100.0</u>	<u>100.00</u>	<u>100.0</u>	<u>100.0</u>				

*Native Peroxide of Tin* is found in Cornwall, in Spain, and in Saxony; it has also been found in Brittany in France, in the East Indies, and in South America. The specific gravity of the native oxide is 7: its primitive crystal is an obtuse octoëdron, of which the modifications are extremely numerous. (W. Phillips, *Geological Transactions*, vol. ii.) In some of the valleys of Cornwall, tin is found in rounded nodules, of various sizes, mixed with pebbles and rounded fragments of rocks. To

separate the tin from the alluvial matter, currents of water are passed over it, and hence these deposits have been called *stream-works*, and the tin ore, *stream-tin*. One of the most extensive of these is a branch of Falmouth Harbour. A modification of stream-tin is called *wood tin*. It usually appears in small banded fragments of globular masses.

PROTOCHLORIDE OF TIN ( $St\alpha + C$ ) is procured by heating together an amalgam of tin and calomel; or more simply, by dissolving tin filings in muriatic acid, evaporating to dryness out of contact of air, and heating the residue till it fuses: it is a gray semi-transparent crystalline solid, fusible below redness, and volatile at a red-heat. Heated in chlorine it burns into perchloride of tin. When the concentrated muriatic solution of tin is cautiously evaporated, it yields crystals of *hydrated protochloride of tin*, containing three equivalents of water. When these crystals are heated, muriatic acid gas and water are evolved, and a compound of protoxide and protochloride remains. The crystals are also decomposed by the affusion of water, which retains muriatic acid and protochloride of tin in solution, and leaves a precipitate composed of 1 equivalent of protoxide, 1 of protochloride, and 2 of water, (Berzelius.) Protochloride of tin consists of

					J. Davy.		
Tin . . . .	1	..	58	..	61.7	..	62.22
Chlorine . .	1	..	36	..	38.3	..	37.78
	1		94		100.0		100.00

PERCHLORIDE OF TIN. ( $St\alpha + 2C$ .) If tin be heated in excess of chlorine, or if amalgam of tin be distilled with corrosive sublimate, a *perchloride* is obtained. The best proportions are six parts of tin, previously combined with one of mercury, and intimately mixed with thirty of corrosive sublimate. The mixture is put into a glass retort with a sufficiently capacious receiver luted to it, and may be distilled over a small charcoal fire. The heat should be slowly raised, to prevent too sudden action. Towards the end of the process a little of the protochloride rises, which the old chemists, from its consistency and appearance, called *Butter of Tin*. Perchloride of tin may also be procured by distilling 8 ounces of finely-powdered tin with 24 of corrosive sublimate. It is a transparent colourless fluid, formerly called *Libavius's Fuming Liquor*: it exhales copious fumes when exposed to a moist air, and produces muriatic acid and oxide of tin. With one-third its weight of water it forms a crystallized hydrate. Its boiling-point is  $250^{\circ}$ ; and, according to Dumas, the density of its vapour is 9.19. It is instantly decomposed by metallic zinc, forming chloride of zinc and a precipitate of metallic tin. It consists of

					J. Davy.		
Tin . . . .	1	..	58	..	44.6	..	42.1
Chlorine . .	2	..	72	..	55.4	..	57.9
	1		130		100.0		100.0

PROTOMURIATE OF TIN, used by dyers, may be obtained by boiling one part of tin with two of muriatic acid; a small portion of insoluble black powder generally remains, together with some undissolved tin. This solution, which is always acid, quickly absorbs oxygen from the air

and from several compounds, and if added to certain metallic solutions, revives or deoxidizes them. It decomposes and precipitates sulphur from sulphurous acid. With a very weak solution of corrosive sublimate it forms a grey precipitate of metallic mercury. Added to a very dilute solution of chloride of platinum it changes its colour to a deep blood-red. With solution of gold it produces a purple precipitate used in painting porcelain, and known under the name of *Purple of Cassius*. It crystallizes from its concentrated solution in prismatic and acicular deliquescent crystals. With infusion of cochineal it produces a purple precipitate; and it is much used to fix and change colours in the art of dyeing and calico-printing. The greater number of vegetable infusions are precipitated by it, in consequence of the insoluble compounds which it forms with the varieties of extractive matter. This muriate of tin is the *Sal Jovis* of old writers. (On the preparation of Muriate of Tin, see Berard, *Ann de Chim.*, lxxviii., 78; and Chaudet, *Ann. de Chim. et Phys.*, iii., 376.)

PERMURIATE OF OXYMURIATE OF TIN may be formed by cautiously dissolving the metal in a nitro-muriatic acid, composed of 2 measures of muriatic acid, 1 of nitric acid, and 1 of water; or by exposing the permuriate to a gentle heat with a small addition of nitric acid. It forms acicular crystals in the upper parts of phials, containing the bichloride imperfectly secured from air; and is directly formed by adding water to the bichloride, which excites much heat, and forms a concrete mass easily fusible and soluble in water. The dyers often prepare this solution by digesting tin-filings in single aquafortis, (nitric acid, sp. gr. 1.3,) to each pound of which, they add about two ounces of common salt or of sal-ammoniac. This compound acid takes up about one-eighth its weight of tin.

IODIDE OF TIN ( $sta+i$ ) may be formed directly by heating the metal with iodine; or indirectly, by adding hydriodic acid to a solution of protochloride of tin. It is an orange-coloured fusible compound, volatile at a high heat, and soluble in water.

IODATE OF TIN has not been examined.

PERIODIDE OF TIN is prepared by dissolving in hydriodic acid the hydrate of the peroxide precipitated by alkalis from the bichloride. It crystallizes in yellow crystals of a silky lustre, which are resolved by boiling water into hydriodic acid and peroxide of tin. (Turner.)

PROTOBROMIDE OF TIN ( $sta+b$ ) is formed by dissolving tin in hydrobromic acid and evaporating to dryness.

PERBROMIDE OF TIN. ( $sta+2b$ .) Metallic tin and bromine act energetically on each other: the metal burns, and a white crystallized compound is obtained, readily fusible and volatile, yielding slight vapours in moist air, and dissolving in water. *Bromate of Tin* has not been examined.

FLUORIDE OF TIN is a soluble and crystallizable compound.

NITRATE OF TIN may be formed by acting upon the metal by dilute nitric acid, or by dissolving the hydrated protoxide in dilute nitric acid; a yellow solution, which will not crystallize, is obtained; exposed to air it absorbs oxygen, and peroxide of tin precipitates. If evaporated, the peroxide falls, and a portion of nitrate of ammonia is formed. It is

evident, therefore, that part of the water, as well as of the acid, are here decomposed; and that the salt is not permanent.

**PROTOSULPHURET OF TIN.** ( $sta + S.$ ) This compound may be procured by heating tin with sulphur; in consequence, however, of the high temperature required for its formation, so much of the sulphur is generally lost, that a mixture of the metal and of the sulphuret is only at first obtained. This mixture may be pulverized, and heated in a retort with its weight of sulphur, in which case the perfect protosulphuret is the result. A protosulphuret of tin is also precipitated, when the salts of the protoxide are mixed with solution of sulphuretted hydrogen. Obtained by the first process, it is a brittle blackish compound of a laminated texture, heavier than tin, fusible at a red-heat, and occasionally forming acicular crystals; it dissolves in muriatic acid with the evolution of sulphuretted hydrogen. It consists of

				J. Davy.		Bergman.	
Tin	. . . 1	.. 58	.. 78.4	.. 78.6	.. 80		
Sulphur	. . . 1	.. 16	.. 21.6	.. 21.4	.. 20		
	1	74	100.0	100.0	100		

**SESQUISULPHURET OF TIN.** ( $sta + 1\frac{1}{2}S.$ ) Berzelius obtained this compound by heating the finely-powdered protosulphuret with one-third its weight of sulphur to dull-redness: it is of a yellowish-gray colour, metallic lustre, and when digested in muriatic acid gives out some sulphuretted hydrogen, and leaves a yellow residue of bisulphuret. Gmelin regards this as a mixture of the protosulphuret and persulphuret.

**BISULPHURET OF TIN.** ( $sta + 2S.$ ) It is formed by heating peroxide of tin with its weight of sulphur. Mr. Woulfe has given formulæ for its production (*Phil. Trans.* 1771); but the following, taken from the *London New Dispensatory* of 1765, answers best. Take 12 oz. of tin and amalgamate it with 6 oz of mercury, reduce it to powder, and mix it with 7 oz. of flowers of sulphur and 6 oz. of sal ammoniac, and put the whole into a glass matrass placed in a sand heat. Apply a gentle heat till the white fumes abate, then raise the heat to redness, and keep it so for a due time. On cooling and breaking the matrass, the bisulphuret of tin is found at the bottom. (See Woulfe's *Paper*, and Aikin's *Dict.*—art. TIN.) According to Berzelius, the use of the mercury is to facilitate the fusion of the tin and its combination with the sulphur, while the sal-ammoniac prevents such increase of temperature as would reduce the tin to the state of protosulphuret. Hence bisulphuret of tin is also formed when a mixture of sulphur, sal ammoniac, and protosulphuret of tin is heated. Bisulphuret of tin is also formed by decomposing perchloride of tin by sulphuretted hydrogen. The extraordinary golden colour and flaky texture of this substance rendered it an object of great interest to the alchemists: it was termed *aurum musivum*, or *mosaic gold*. When well made it is in very soft golden flakes, very friable, and adhering to the fingers. It is insoluble in the acids, except in nitro-muriatic acid: it is soluble in caustic potassa, but not without partial decomposition. This curious compound is much used for ornamental work, under the name of *bronze-powder*, especially

by the manufacturers of paper-hangings: it is chiefly imported from Germany. It consists of

				J. Davy.		Berzelius.	
Tin . . . .	1 . .	58 . .	64.4 . .	63.6 . .	65 . .	65 . .	65 . .
Sulphur . . . .	2 . .	32 . .	35.6 . .	36.4 . .	35 . .	35 . .	35 . .
		<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
		1	90	100.0	100.0	100	100

HYPOSULPHITE OF TIN has not been examined. Protochloride of tin forms no precipitate with the alkaline hyposulphites.

SULPHITE OF TIN is formed by digesting the protoxide in sulphurous acid, but the salt has not been examined.

SULPHATES OF TIN. When tin is boiled in sulphuric acid, a solution is obtained which deposits white acicular crystals of *protosulphate of tin*. It is also precipitated by pouring sulphuric acid into protochloride of tin. The hydrated peroxide of tin is also soluble in sulphuric acid.

PHOSPHURET OF TIN may be formed by dropping phosphorus into melted tin. It is of a silvery colour, sectile, and somewhat ductile. When its filings are sprinkled upon hot coals the phosphorus burns.

PHOSPHITE OF TIN is produced, according to Rose, by mixing protochloride of tin with protochloride of phosphorus saturated by ammonia. (*Ann. de Chim. et Phys.*, xxxv. 218.)

PHOSPHATE OF PROTOXIDE OF TIN is formed by adding phosphate of soda to the protomuriate. It is a white powder, not soluble in water, and fuses at a red-heat into an opaque white enamel.

CARBONATE OF TIN. When carbonate of potassa is added to protomuriate of tin, a white precipitate ensues, which, when washed and dried, loses carbonic acid, so that no permanent carbonate appears to exist.

BORATE OF TIN is an insoluble white powder.

FERROCYANURET OF TIN. Ferrocyanuret of Potassium produces a white precipitate in solution of protochloride of tin.

ALLOYS OF TIN. With *potassium* and *sodium* tin forms brittle white alloys. Its alloy with *manganese* is not known. It does not readily combine with *iron*, but *tin-plate* (on the manufacture of which see Parkes' *Essays*), may be considered as an imperfect alloy of those metals. With *zinc* it forms a hard brittle alloy. (On the alloys of tin, see Dussaussy, *Ann. de Chim. et Phys.*, v., and Chaudet, in the same work, v. and vii.)

Tin medals are *bronzed* by being first well cleaned, wiped, and washed over with a solution of 1 part of protosulphate of iron, and 1 of sulphate of copper, in 20 of water: this gives a gray tint to the surface; they are then brushed over with a solution of 4 parts of verdigris in 11 of distilled vinegar; left for an hour to dry; and polished with a soft brush and colcothar.

CHARACTERS OF THE SALTS OF TIN. The salts of the *protoxide* have a highly astringent and disagreeable taste; they are mostly colourless, and are precipitated white by ferrocyanuret of potassium, and brown by hydrosulphurets of the alkalis: white by caustic soda and potassa, and excess of alkali redissolves the precipitate. They reduce the persalts of many metals to the state of protosalts; such as the persalts of copper, iron, and mercury: with dilute solution of gold they give a red or purple precipitate. Succinates and benzoates of the alkalis give white, and tincture

of galls yellow, precipitates. The salts of the *peroxide* are colourless and do not reduce the other metallic persalts; heated with nitric acid, peroxide of tin is generally separated: they are precipitated white by ferrocyanuret of potassium, and dirty yellow by the hydrosulphuretted alkalis.

Protochloride of tin is decomposed by zinc and by cadmium, which quickly and entirely precipitate tin in a metallic state. Lead immersed in a solution of the protochloride of tin becomes covered with spicular crystals of the latter metal, which prevent further action. Pure and anhydrous perchloride of tin is not decomposed by any of the metals: if water be present it is acted upon as the protochloride. The alkaline solution of oxide of tin is reduced by zinc and cadmium, and less perfectly by lead.

## § XII. CADMIUM.

THIS metal was discovered in 1817, by the late Professor Stromeyer, of Göttingen, in examining into the cause of the yellow colour of certain oxides of zinc: he called it *Cadmium*, from *καδμεία*, a term formerly applied both to calamine, and to the substance which sublimes from the furnace during the manufacture of brass. It is contained in certain ores of zinc, and especially in the *black fibrous blende* of Bohemia. It has been detected by Dr. Clarke in the *calamine* of Derbyshire and Somersetshire, and in the zinc of commerce, (*Ann. of Phil.*, xv., 272, and New Series, iii., 123,) and Mr. Herapath found it in considerable proportion in the sublimate which, in the process for obtaining zinc, rises before that metal, forming what the workmen call the *brown blaze*. (*Ann. of Phil.*, iii., 435.) It may be procured by digesting the ore in muriatic acid, by which a mixed muriate of zinc and cadmium is obtained: it should be evaporated to dryness, to drive off excess of acid, and re-dissolved in water. Immerse a plate of iron into this solution, to separate all that may be thus precipitated, and afterwards filter the liquor into a platinum capsule containing a piece of zinc. The cadmium will coat over the surface of the capsule, and adhere so firmly to it, that it may be washed, and thus freed from any remaining solution of zinc. Muriatic acid dissolves the precipitate with effervescence, and from this solution it is thrown down white by the alkalis, and yellow by sulphuretted hydrogen. (Wollaston.) It may be reduced to the metallic state by mixing the oxide with charcoal, and applying a red-heat in a tube or retort, when the cadmium, being volatile at that temperature, sublimes.

Stromeyer separates cadmium from the ores containing it, by digesting them in dilute sulphuric acid, and passing sulphuretted hydrogen through the acidulous solution. He washes the precipitate thus formed, dissolves it in muriatic acid, and expels the excess of acid by evaporation. He then redissolves the residue in water, precipitates by carbonate of ammonia, of which an excess is added, for the purpose of retaining the oxides of zinc and copper in solution; the remaining carbonate of cadmium is washed, dried, and heated with lampblack, by which it is easily reduced.

The physical properties of cadmium closely resemble those of tin, but

it is rather harder and more tenacious; its specific gravity is 8.60, and somewhat exceeds 8.69 after hammering. It fuses at a temperature a little below that required by tin, and distils over at a heat somewhat below redness, condensing into metallic globules: its vapour is inodorous. Air does not act upon it except when heated, when it forms an orange-coloured oxide, not volatile, and easily reducible. Its equivalent is 56. (55.8 Turner.)

PROTOXIDE OF CADMIUM (*cad* + *o*) or CAD: This, which is the only known oxide, may be obtained by burning the metal in oxygen, or by dissolving it in dilute nitric acid, and precipitating it in the state of carbonate, which is then washed, dried, and ignited. It is of a reddish-brown or orange colour, and is neither volatile nor fusible; but when mixed with carbonaceous matter it appears volatile, in consequence of its easy reduction, and the burning off of the separated cadmium. When thrown down from its solutions by alkalies it forms a white *hydrate*, soluble in excess of ammonia, but insoluble in potassa or soda.

Oxide of cadmium consists of

						Stromeyer.		John.	
Cadmium . . .	1	..	56	..	87.5	..	87.45	..	90
Oxygen . . .	1	..	8	..	12.5	..	12.55	..	10
	1		64		100.0		100.00		100.

CHLORIDE OF CADMIUM (*cad* + *c*) is formed by dissolving the hydrated oxide in muriatic acid: on evaporation, small prismatic crystals are obtained, very soluble in water, and efflorescent in a dry atmosphere. These crystals readily fuse into a crystalline mass, which is *chloride of cadmium*: at a very high temperature it is volatile, and concretes in the form of a lamellar sublimate. It consists of

						Stromeyer.	
Cadmium . . .	1	..	56	..	60.8	..	61.38
Chlorine . . .	1	..	36	..	39.2	..	38.62
	1		92		100.0		100.00

IODIDE OF CADMIUM (*cad* + *i*) is a colourless crystallizable compound, fusible, and resolved at a high temperature into iodine and cadmium. It is easily formed by heating cadmium with iodine, or mixing them in a moist state. Its alcoholic or aqueous solution yields large six-sided tables, of a pearly lustre. It consists of

						Stromeyer.	
Cadmium . . .	1	..	56	..	30.94	..	30.541
Iodine . . .	1	..	125	..	69.06	..	69.459
	1		181		100.00		100.000

FLUORIDE OF CADMIUM is a difficultly-soluble compound.

NITRATE OF CADMIUM (*CAD* + *n'*) forms radiated acicular crystals, which are deliquescent, and soluble in alcohol. They consist of

						Stromeyer.	
Oxide of cadmium . . .	1	..	64	..	41.56	..	42.15
Nitric acid . . .	1	..	54	..	35.07	..	35.78
Water . . .	4	..	36	..	23.37	..	22.07
	1		154		100.00		100.00

SULPHURET OF CADMIUM (*cad* + *S*) is obtained in the form of a bright-yellow powder, insoluble in pure potassa, by precipitating the solutions of the metal with sulphuretted hydrogen. It is also formed by heating cadmium, or its oxide, with sulphur, and concretes, on cooling, into a yellow lamellar mass. It dissolves with the evolution of sulphuretted hydrogen in concentrated muriatic acid, and is not volatile at a white heat. It is composed of

						Stromeyer.
Cadmium . . .	1	..	56	..	77.77	.. 78.02
Sulphur . . .	1	..	16	..	22.23	.. 21.98
	1		72		100.00	100.00

HYPOSULPHATE OF CADMIUM is a very soluble deliquescent salt. (Heeren.)

SULPHATE OF CADMIUM (*CAD* + *S'*) forms transparent prismatic crystals, much resembling those of sulphate of zinc: they are efflorescent, and very soluble in water: gently heated, they lose water of crystallization, and at a higher temperature a part of the acid escapes, and a basic sulphate, difficultly soluble, and crystallizing in scales, remains. The crystals of the sulphate contain

						Stromeyer.
Oxide of cadmium . .	1	..	64	..	45.72	.. 45.956
Sulphuric acid . . .	1	..	40	..	28.57	.. 28.523
Water . . . . .	4	..	36	..	25.71	.. 25.521
	1		140		100.00	100.000

PHOSPHURET OF CADMIUM (*cad* + *p*) is a gray, brittle compound, with a feeble metallic lustre, and very difficult of fusion.

PHOSPHATE OF CADMIUM is an insoluble white powder, formed by adding neutral phosphate of soda to a soluble salt of cadmium. It consists, according to Stromeyer, of 69.2 oxide of cadmium, and 30.8 phosphoric acid: the equivalents would give 64 + 36.

CARBONATE OF CADMIUM (*CAD* + *car'*) is a white insoluble anhydrous powder, which loses its acid at a red-heat, and consists of

						Stromeyer.
Oxide of cadmium . .	1	..	64	..	74.42	.. 74.547
Carbonic acid . . .	1	..	22	..	25.58	.. 25.453
	1		86		100.00	100.000

BORATE OF CADMIUM is an insoluble white powder, containing, according to Stromeyer, 72.1 oxide, 27.9 acid; numbers which are irreconcilable with the equivalents.

ALLOYS OF CADMIUM. Cadmium combines readily with other metals, forming brittle alloys, from which the cadmium is expelled by a high heat: few of them have been examined.

THE SALTS OF CADMIUM are white and colourless, and mostly soluble in water: the solution has a nauseous metallic taste; they are precipitated *white* by caustic and carbonate alkalis, and by ferrocyanuret of potassium; and *yellow* by sulphuretted hydrogen: they are not affected by tincture of galls. Zinc is the only metal which throws down metallic cadmium. The scarcity of cadmium prevents its application to useful purposes, otherwise its malleability would render it available in the arts, and its oxide would perhaps be a good pigment. Its applications in medicine would probably be analogous to those of zinc.



## § XIII. COBALT.

THE following account of the discovery of cobalt is given by Dr. Thomson. (*Inorg. Chem.*, i., 536.)

A mineral called *cobalt*\*, of a gray colour, and very heavy, has been used in different parts of Europe, since the 15th century, to tinge glass of a blue colour. But the nature of this mineral was altogether unknown till it was examined by Brandt, in 1733. This celebrated Swedish chemist obtained from it a new metal, to which he gave the name of *cobalt*. (*Acta Upsal.*, 1733 and 1742.) Lehmann published a very full account of everything relating to this metal in 1761. (*Cadmia-logia, oder Geschichte des Farben-Kobolds.*) Bergman confirmed and extended the discovery of Brandt in different dissertations published in the year 1780. (*Opusc.*, ii., 444, 501, and iv., 371.) Scarcely any further addition was made to our knowledge of this metal till 1798, when a paper on it was published by Mr. Tassaert. (*Ann. de Chim.*, xxviii., 101.) In the year 1800, a new set of experiments were made upon it by the School of Mines at Paris, in order to procure it perfectly pure, and to ascertain its properties when in that state. (Fourcroy, *Discours Préliminaire*, p. 114.) In 1802, a new series of trials was published by Thenard, which throw considerable light on its combinations with oxygen. (*Ann. de Chim.*, xlii., 210.) And in 1806, Mr. Proust published a set of experiments upon the same subject. (*Ann. de Chim.*, lx., 260.) Considerable attention has been lately paid to the purification of this metal; but hitherto no one seems to have been fortunate enough to hit upon a method altogether free from objections.

The *native* combinations of cobalt are the oxide, and compounds of the metal with iron, nickel, arsenic, and sulphur. It is also found combined with arsenic acid. In the white and gray cobalt-ores, the metal is combined with iron, and with arsenic. The ore commonly called *glance cobalt*, from Tunaberg, in Sweden, is a sulpho-arseniuret of cobalt. Some of the varieties are crystallized in cubes, octoëdrons, and dodecaëdrons.

\* The word *cobalt* seems to be derived from *cobalus*, which was the name of a spirit that, according to the superstitious notions of the times, haunted mines, destroyed the labours of the miners, and often gave them a great deal of unnecessary trouble. The miners probably gave this name to the mineral out of joke, because it thwarted them as much as the supposed spirit, by exciting false hopes, and rendering their labour often fruitless; for as it was not known at first to what use the mineral could be applied, it was thrown aside as useless. It was once customary in Germany to introduce into the church-service a prayer that God would preserve miners and their works from *kobalts* and *spirits*. (See Beckmann's *History of Inventions*, ii., 362.) Mathesius, in his tenth sermon, where

he speaks of *cadmia fossilis* (probably cobalt ore), says, "Ye miners call it *cobalt*; the Germans call it the black devil and the old devil's whores and hags, old and black *kobel*, which by their witchcraft do injury to people and to their cattle." Lehmann, Paw, Delaval, and several other philosophers, have supposed that *smalt* (oxide of cobalt melted with glass and pounded) was known to the ancients, and used to tinge the beautiful blue glass still visible in some of their works; but we learn from Gmelin, who analyzed some of these pieces of glass, that they owe their *blue* colour, not to the presence of *cobalt*, but of *iron*. According to Lehmann, cobalt ore was first used to tinge glass blue by Christopher Schurer, a glassmaker at Platten, about the year 1540.

The *red ore* is an arseniate. The finest specimens are the produce of Saxony. Cobalt has also been detected, by Stromeyer, in several specimens of metallic iron.

Cobalt is never employed in the metallic state, so that the processes for its reduction are generally carried on upon a small scale, and confined to the experimental laboratory.

To obtain pure cobalt, the cobalt of commerce, in fine powder, may be calcined with four parts of nitre, and washed in hot water, by which much arsenic is separated: then digest it in dilute nitric acid, and immerse a plate of iron into the solution, which will separate the copper; filter, and evaporate to dryness; digest the dry mass in liquid ammonia and filter; expel the excess of ammonia from the filtered liquor by heat, taking care not to produce a precipitate, and then add solution of potassa, which throws down oxide of nickel; filter immediately, and boil, which will occasion the separation of oxide of cobalt; this, ignited with charcoal, furnishes the pure metal. In this process the first calcination with nitre often requires two or three repetitions in order to get rid of the whole of the arsenic, which adheres to cobalt with much obstinacy.

When the ores of cobalt, or the impure oxide called *Zaffre*, are dissolved in muriatic acid by the aid of a little nitric acid, and sulphuretted hydrogen passed through the solution, the arsenic is precipitated: the filtered liquor may then be boiled with a little nitric acid to peroxidize the iron, and precipitated by carbonate of potassa: the precipitate, when well washed, is to be digested in oxalic acid, which leaves an insoluble oxalate of cobalt: this may be decomposed at a high heat. When dry hydrogen gas is passed over oxide of cobalt, it is also reduced.

Cobalt is of a reddish-gray colour, brittle, and difficultly fusible. Its specific gravity, according to Bergman, is 7.7; according to Turner, 7.834. Tassaert and Lampadius place it at 8.5 and 8.7. It is feebly magnetic. Its equivalent is 30. (29.5 Gmelin and Turner.)

COBALT AND OXYGEN unite in two proportions. PROTOXIDE OF COBALT (*cob* + *o*) or *CoB*, is formed by adding potassa to the nitrate, and washing and drying the precipitate; it appears very dark blue or nearly black. By exposure to heat and air it absorbs an additional portion of oxygen, and is thus converted into black *peroxide*. The protoxide, when recently precipitated and moist, is *blue*; and, if left in contact of water, becomes a *red hydrate*; and afterwards of a dingy green by absorbing oxygen.

The protoxide may also be obtained by heating the carbonate of cobalt out of contact of air; it is then of a greenish-gray colour. It is recognised by the facility with which it imparts a blue tint to vitrifiable compounds and to white enamel. It consists of

						Rothoff.	Berthier.			
Cobalt	. .	1	. .	30	. .	78.9	. .	78.67	. .	78.75
Oxygen	. .	1	. .	8	. .	21.1	. .	21.33	. .	21.25
		<u>1</u>		<u>38</u>		<u>100.0</u>		<u>100.00</u>		<u>100.00</u>

PEROXIDE OF COBALT; SESQUIOXIDE OF COBALT. (*cob* +  $1\frac{1}{2}o$ .) When the finely-divided metal, or the protoxide, are heated in the air, they absorb oxygen, and acquire a dark-brown colour, forming an oxide intermediate between the peroxide and protoxide, and probably of indefinite composition; but according to Hess (*Poggend.* xxvi., 542), consisting of

( $3CO + 4O$ ). When chlorine is passed through a mixture of the hydrated protoxide and water, or when a solution of chloride of cobalt is decomposed by chloride of lime, a black precipitate falls, which is the *hydrated peroxide*, and which may be deprived of water by very cautious drying at a high temperature; it is then black, and insoluble in dilute acids; it does not form salts; when acted on by muriatic acid it evolves chlorine, and yields chloride of cobalt. It consists of

					Rothoff.
Cobalt . . .	1	..	30	..	71.8
Oxygen . . .	$1\frac{1}{2}$	..	12	..	28.5
	1		42		100.0
					71.08
					28.92
					100.00

CHLORIDE OF COBALT. (*cob + c.*) Cobalt burns when heated in chlorine, and forms *chloride of cobalt*. When muriate of cobalt is evaporated to dryness, and the residuum heated to redness out of the contact of air, a substance of a blue colour and micaceous texture is obtained, which is a pure chloride of cobalt. It dissolves perfectly in water, forming a pink solution. The anhydrous chloride consists of

					Brandé.
Cobalt . . .	1	..	30	..	45.4
Chlorine . . .	1	..	36	..	54.6
	1		66		100.0
					47.75
					52.25
					100.00

When the blue anhydrous chloride of cobalt is dissolved in water it yields a pink solution, which if duly diluted, and written with, becomes invisible when dry; but if gently heated, the writing appears in brilliant blue, which soon vanishes as the paper cools, in consequence of the salt absorbing the aërial moisture. This solution has been termed *Hellot's sympathetic ink*. Dr. Thomson states that it was first made known by Waitz, in 1705; a second time by Teichmeyer, in 1731; and, lastly, by Hellot, in 1737. (*Mém. Paris.*) If it contain copper, nickel, or iron, the writing appears green; hence, in what are termed *magic landscapes*, the sky is tinted with solution of pure chloride of cobalt, and the trees and grass with that which is cupreous. By careful evaporation, the solution of this chloride forms red crystals, in the form of oblique rhombic prisms (Brooke, *Ann. of Phil.*, 2nd series, vii., 365), composed of one proportional of the chloride and five of water.

IODIDE OF COBALT remains unexamined. No precipitate is produced in solutions of cobalt either by hydriodic acid, or iodide of potassium; or by iodic acid, or iodate of potassa.

BROMIDE OF COBALT has not been examined.

FLUORIDE OF COBALT. When oxide of cobalt is digested in hydrofluoric acid, a pink solution is obtained, which yields crystals on evaporation, difficultly soluble in water.

NITRATE OF COBALT. With nitric acid the oxide of cobalt furnishes a brownish-red deliquescent salt in irregular rhombic crystals, consisting, according to Dr. Thomson, of 1 proportional of oxide of cobalt, 1 of nitric acid, and 6 of water.

AMMONIATED OXIDE OF COBALT; COBALTATE OF AMMONIA. It is doubtful whether any binary compound of ammonia and oxide of cobalt exists. Salts of cobalt with excess of acid are not precipitated by ammonia,

nor by ammoniacal salts, because double salts are formed. From a neutral solution of cobalt, ammonia throws down a portion of oxide in the form of blue hydrate, which remains unchanged provided air be excluded; but, if air has access, oxygen is absorbed, and the precipitate first becomes green, and then dissolves into a brown fluid, which appears to be a compound of *cobaltate of ammonia* with the other ammoniacal salt. L. Gmelin supposes the *cobaltic acid* to consist of 1 equivalent of cobalt and 2 of oxygen; its ammoniacal solution is apt to deposit peroxide of cobalt, in which case it also gives out nitrogen.

SULPHURET OF COBALT is formed by heating cobalt or its oxide with sulphur. It is yellowish-white, and contains, according to Proust, 71.5 cobalt, 28.5 sulphur. A hydrous sulphuret of cobalt is thrown down by sulphuretted hydrogen from perfectly neutral solutions of cobalt.

SULPHITE AND HYPOSULPHITE OF COBALT have not been examined.

HYPOSULPHATE OF COBALT forms, according to Heeren, a red saline mass, very soluble, but not deliquescent: he obtained it by the decomposition of sulphate of cobalt by hyposulphate of baryta.

SULPHATE OF COBALT (COB + S') forms oblique rhombic prisms, like sulphate of iron, (Brooke, *Ann. of Phil.*, vi. 120, 2nd. series,) soluble in 24 parts of water at 60°, and insoluble in alcohol. It may be made by dissolving the newly precipitated protoxide or carbonate of cobalt in sulphuric acid diluted with its bulk of water.

When dried at a temperature of 500°, the crystals fall into a blue powder, which, in a bright red-heat, fuses, and gives out sulphuric acid, leaving a black oxide. The blue powder is the *anhydrous sulphate of cobalt*, perfectly soluble in water, and forming a pink solution; it is slightly deliquescent, and becomes lilac-coloured by exposure to air. It consists of

						Rothoff.		Brande.	
Oxide of Cobalt	1	..	38	..	48.7	..	47.89	..	50
Sulphuric acid	1	..	40	..	51.3	..	52.11	..	50
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		78		100.0		100.00		100

The crystals consist of

						Bucholz.	Mitscherlich.	Proust.			
Anhydrous sulphate of cobalt	1	.	78	.	59.1	.	56	.	57.3	.	58
Water		.	6	.	54	.	44	.	42.7	.	42
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		132		100.0		100		100.0		100

When hydrogen gas is passed over sulphate of cobalt, heated to redness in a tube, sulphurous acid and water are evolved, and there remains from 100 parts of dry sulphate 53.62 of a dark-gray agglutinated powder, composed of 1 equivalent of oxide and 1 of sulphuret of cobalt. When sulphuretted hydrogen is passed over 100 parts of this compound, at a red-heat, 117 parts of *sesquisulphuret of cobalt* are obtained. (Arfwedson, *Poggend.*, i. 64.) When this sesquisulphuret is digested in muriatic acid, or when 1 part of carbonate of cobalt, and 1½ of sulphur are heated (below redness,) till water, carbonic acid, sulphurous acid, and excess of sulphur cease to pass off, there remains a black *bisulphuret of cobalt*. (Setterberg.)

BISULPHATE OF COBALT is formed by digesting the sulphate in excess

of acid; the solution affords prismatic efflorescent crystals, composed of 1 proportional of protoxide of cobalt, 2 sulphuric acid, and 3 water.

AMMONIO-SULPHATE AND POTASSA-SULPHATE OF COBALT. Sulphate of cobalt forms triple compounds with ammonia and with potassa, which have not been minutely examined. If it contain nickel, the crystals are of a greenish tinge, but pink when the cobalt is pure.

HYDROSULPHURETTED OXIDE OF COBALT is precipitated from the muriate by hydrosulphuret of ammonia, of a black colour. Sulphuretted hydrogen does not throw down cobalt from solutions with excess of acid; but it occasions precipitates in those which are perfectly neutral.

PHOSPHURET OF COBALT is a white brittle compound.

HYPOPHOSPHITE OF COBALT forms, according to Rose, octoëdral efflorescent crystals containing 49.35 *per cent.* of water of crystallization.

Nothing is known respecting the *Phosphite of Cobalt*.

PHOSPHATE OF COBALT may be formed by double decomposition, as by adding phosphate of soda to chloride of cobalt; it is insoluble in water, of a lilac colour, and soluble in excess of phosphoric acid; if mixed with two or three parts of pure alumina, and exposed in a covered crucible to a full white-heat, it produces a beautiful blue colour, which may sometimes be employed by painters as a substitute for ultramarine: a pure salt of cobalt free from nickel, pure alumina free from iron, and a high heat, are essential to the production of a fine blue. This compound, from its discoverer, is sometimes called *Thenard's blue*.

CARBONATE OF COBALT (COB + CAR') is formed by decomposing the nitrate, muriate, or sulphate of cobalt by carbonate of potassa, or soda; a purple powder is precipitated, becoming pink when dried, and readily soluble with effervescence in the acids. Heated in close vessels it gives off carbonic acid, and a gray protoxide of cobalt remains. It dissolves in excess of carbonic acid, and in alkaline carbonates.

AMMONIO-CARBONATE OF COBALT. Carbonate of cobalt is readily soluble in solution of carbonate of ammonia, forming a bright pink liquid.

CYANURET OF COBALT. Hydrocyanic acid, added to acetate of cobalt, throws down the whole of the metal in the form of cyanuret.

FERROCYANURET OF COBALT. Ferrocyanuret of potassium gives a greenish yellow, or gray precipitate; and ferrosesquicyanuret a brown precipitate, in solutions of cobalt: these precipitates are insoluble in muriatic acid.

COBALTOCYANURET OF POTASSIUM. Cyanuret of cobalt is dissolved in a solution of cyanuret of potassium; or hydrocyanic acid is added to a solution of cyanuret of cobalt, or of carbonate of cobalt, in potassa, till it no longer reddens turmeric; on evaporation, transparent shining prismatic crystals are obtained, which are neutral to vegetable colours, decrepitate when heated, and then fuse into a dark olive-green liquid. This salt is easily soluble in water, and the solution is nearly colourless. The pink precipitate which it produces in the salts of cobalt, is, perhaps, analogous to prussian-blue. (Leopold Gmelin.) This salt is anhydrous, and consists of

Potassium	.	.	3	..	120	..	35.8	..	35.23
Cobalt	.	.	2	..	60	..	17.9	..	17.19
Cyanogen	.	.	6	..	156	..	46.3	..	47.58
			<hr/>		<hr/>		<hr/>		<hr/>
			1		336		100.0		100.00

L. Gmelin.

**SULPHOCYANURET OF COBALT.** Sulphate of cobalt is added to an alcoholic solution of sulphocyanuret of potassium; sulphate of potassa falls, and the blue solution yields prismatic crystals which deliquesce in the air into a liquid, at first violet-coloured, then red, and yielding a nearly colourless solution in water, which, on the addition of alcohol, again becomes blue. (Grotthuss, Gilbert's *Ann.*, lxi. 70.)

**BORATE OF COBALT.** Solution of borax occasions a pink precipitate in solution of chloride of cobalt, which is a *borate of cobalt*, and which produces a beautiful blue glass when fused.

The *alloys of cobalt* are unimportant. The chief use of cobalt is in the state of *oxide* as a colouring material for porcelain, earthenware, and glass; it is principally imported from Germany in the state of *zaffre*, and *smalt* or *azure*. *Zaffre* is prepared by calcining the ores of cobalt, by which sulphur and arsenic are volatilized, and an impure oxide of cobalt remains, which is mixed with about twice its weight of finely-powdered flints. *Smalt* and *azure blue* are made by fusing *zaffre* with glass; or by calcining a mixture of equal parts of roasted cobalt ore, common potash, and ground flints. In this way a blue glass is formed, which, while hot, is dropped into water, and afterwards reduced to a very fine powder.

**CHARACTERS OF THE SALTS OF COBALT.** Solution of potassa produces a blue precipitate in solutions of cobalt which becomes green, and if boiled, or long kept, dirty red. It is not redissolved by excess of potassa. Ammonia, forms a blue precipitate in solutions of cobalt, which, on its further addition becomes green, and mostly dissolves: this solution becomes brown by exposure to air. Carbonate of ammonia produces a red precipitate, which dissolves in muriate of ammonia. Hydrosulphuret of ammonia produces a black precipitate even when the cobaltic solution is excessively dilute. Those salts of cobalt which are insoluble in water, are nearly all soluble in dilute sulphuric or muriatic acid, and are generally thrown down by ammonia, and blackened by hydrosulphuret of ammonia. When no precipitate is produced in an acidulated metallic solution by sulphuretted hydrogen gas, while at the same time a black precipitate is produced in the neutral or alkaline solution, by hydrosulphuret of ammonia, scarcely any other metal than cobalt, nickel, or iron, can be present. (H. Rose.) Before the blow-pipe cobalt and its compounds colour borax and microcosmic-salt blue. By soda or charcoal they are reduced to a gray magnetic powder which is metallic cobalt. (Berzelius.) Cobalt is not thrown down in the metallic state by any of the other metals.

#### § XIV. NICKEL.

NICKEL was discovered by Cronstedt, in 1751. Its ores were termed by the German miners, *kupfernichel*, or "false copper." It is found *native*, and combined with arsenic, and with arsenic acid. It is procured pure by the following process:—Dissolve the impure metal, sold under the name of *Speiss*, in sulphuric acid, by adding the quantity of nitric acid necessary to produce the solution. Concentrate this solution, and set it aside; fine green crystals of sulphate of nickel make their appearance. Proceed in this manner till you have obtained a sufficient quantity of crystals. Dissolve them in water, and crystallize a second time. If they

be now dissolved in water, and sulphuretted hydrogen passed through the solution to precipitate any copper or arsenic that may be present, and recrystallized, they furnish a solution from which a nearly pure oxide of nickel is thrown down by potassa: it may, however, still retain cobalt, which is perhaps most easily separated by diffusing the hydrated precipitate through water, and subjecting it to a current of chlorine, by which the cobalt is thrown down (with some nickel) in the form of peroxide, and a solution of chloride of nickel is obtained, from which the pure hydrated oxide of nickel may now be thrown down, by potassa; or, if intended for the production of the metal, by oxalic acid in the state of *oxalate*; which is then dried, and intensely heated in a covered crucible: it affords a button of pure nickel: the metal may also be obtained by exposing a mixture of lampblack and oxide of nickel, made into a paste with oil, to a heat gradually raised to whiteness.

Nickel is a white brilliant metal, which acts upon the magnetic needle, and is itself capable of becoming a magnet. Its magnetism is more feeble than that of iron, and vanishes at a heat somewhat below redness. It is ductile and malleable\*: its specific gravity = 8.5. It is not oxydized by exposure to air or moisture at common temperatures, but when heated in the air it acquires various tints, like steel; at a red heat it becomes coated by a gray oxide: before the oxygen blowpipe it burns with sparks, somewhat like iron: its equivalent number, deduced from various analyses of its compounds, is between 27 and 30. I have assumed it at 28. (29.5, Gmelin and Turner; 26, Thomson.)

PROTOXIDE OF NICKEL, ( $NiC + O$ .) or  $NiC$ , is obtained by adding potassa to the solution of the pure nitrate or sulphate; a precipitate falls of a pale-green colour, which is a *hydrated protoxide*; this, heated to redness, affords a gray protoxide. The carbonate, or nitrate of nickel, heated to redness, also afford the protoxide in the form of a gray powder: when intensely heated it becomes green. It is not magnetic. This oxide, in the state of hydrate, easily dissolves in ammonia, forming a sapphire-blue solution; this property is often made use of to separate oxides of nickel and iron, the latter being insoluble in ammonia. Protoxide of nickel consists of

					Klaproth.					Richter.			Thomson.			Rothoff.
Nickel	1	..	28	..	77.77	..	77	..	77.82	..	78	..	78	..	78.55	
Oxygen	1	..	8	..	22.23	..	23	..	22.18	..	22	..	22	..	21.45	
	<u>1</u>		<u>36</u>		<u>100 00</u>		<u>100</u>		<u>100.00</u>		<u>100</u>		<u>100</u>		<u>100.00</u>	

PEROXIDE OF NICKEL. ( $NiC + 1\frac{1}{2} O$ .) If excess of chlorine be passed through a mixture of the hydrated oxide and water, a black powder is gradually formed, which, when acted upon by the acids, evolves oxygen, and returns to the state of protoxide. It is not, therefore, a salifiable base. It consists of

							Rothoff.		Lassaigne.	
Nickel	. .	1	..	28	..	70	..	70.95	..	71.43
Oxygen	. .	$1\frac{1}{2}$	..	12	..	30	..	29.05	..	28.57
		<u>1</u>		<u>40</u>		<u>100</u>		<u>100.00</u>		<u>100.00</u>

\* I have a Bavarian coin struck in nickel; the impression of the die is very perfect.

CHLORIDE OF NICKEL. (*NiC + C.*) When finely-divided nickel is heated in chlorine, the gas is absorbed, and an olive-coloured *chloride* results. This compound may also be obtained by dissolving oxide of nickel in muriatic acid, evaporating to dryness, and heating the residue to redness in a glass tube; it then remains in the form of a yellow lamellar substance, which, when dissolved in water, leaves on evaporation a confusedly crystalline mass, of an apple-green colour and sweetish taste. It forms a double salt with muriate of ammonia. Chloride of nickel consists of

Nickel	. . . .	1	. .	28	. .	43.7
Chlorine	. . . .	1	. .	36	. .	56.3
		1		64		100.0

IODIDE OF NICKEL may be formed by adding solution of iodide of potassium to sulphate or nitrate of nickel; it is of a greenish-yellow colour, and insoluble.

FLUORIDE OF NICKEL, obtained by dissolving the hydrated oxide in hydrofluoric acid, yields green irregular crystals, and forms double salts with ammonia and with potassium.

NITRATE OF NICKEL is a green deliquescent salt, difficultly crystallizable in rhomboids. The analyses of this salt are much at variance, but it probably consists of 1 atom of oxide and 1 of acid. The crystals contain 3 proportionals of water; or 5, according to Thomson. (*First Lines*, ii., 334); they are soluble in 2 parts of water at 60°, and also dissolve in alcohol. By adding excess of ammonia to nitrate of nickel, and evaporating, green crystals of *ammonio-nitrate of nickel* are obtained, the solution of which affords no precipitate with potassa or soda.

AMMONIA AND OXIDE OF NICKEL. When hydrated oxide of nickel is digested in ammonia it readily dissolves and forms a deep-blue solution, the shade of which is paler when the oxide predominates. When heated, it deposits granular crystals of hydrated oxide: exposed to air, it gradually deposits *ammonio-carbonate of nickel*. The fixed alkalis throw down oxide of nickel, combined with the alkali used.

SULPHURET OF NICKEL, (*NiC + S*) may be formed by fusion, or by heating oxide of nickel with sulphur. When sulphuretted hydrogen is passed into a perfectly neutral solution of nickel, a part of the metal falls in the form of a black sulphuret, or hydrosulphuretted oxide; if the solution be acid, the metal is not thus precipitated: hence the method of separating nickel from certain other metals, such as copper and arsenic, the precipitation of which is not prevented by excess of acid. A sulphuret of nickel is also thrown down, when the soluble salts of nickel are decomposed by sulphuret of potassium. There is also a *native sulphuret of nickel*, which occurs in capillary filaments, of a yellow-gray colour. It is the *hair-pyrites* of the Germans. Sulphuret of nickel consists of

					Arfwedson.	E. Davy.	Rose. <i>Native.</i>				
Nickel	1	. .	28	. .	63.5	. .	64.35	. .	66	. .	64.8
Sulphur	1	. .	16	. .	36.5	. .	34.26	. .	34	. .	35.2
	1		44		100.0		98.61		100		100.0

Neither the *Hyposulphite*, the *Sulphite*, nor the *Hyposulphate* of Nickel have been examined.

SULPHATE OF NICKEL (*NiC + S'*) is formed by digesting the oxide or



carbonate in dilute sulphuric acid. A bright-green solution is formed, which affords prismatic crystals, the form of which varies, depending, according to Phillips and Cooper (*Ann. of Phil.*, xxii., 489), upon variation in the water of crystallization; soluble in about 3 parts of water at 60°, and efflorescent by exposure. Their taste is sweet and astringent. They are insoluble in alcohol and in ether. Exposed to heat, they crumble down into a yellow powder. This salt is also obtained by heating common nickel in sulphuric acid, with the occasional addition of nitric acid; though it is seldom pure when thus prepared. Anhydrous sulphate of nickel consists of

					Berthier.	Tupputi.				
Oxide of nickel	. .	1	. .	36	. .	47.4	. .	47.8	. .	46.6
Sulphuric acid	. .	1	. .	40	. .	52.6	. .	52.2	. .	53.4
		<u>1</u>		<u>76</u>		<u>100.0</u>		<u>100.0</u>		<u>100.0</u>

The crystallized sulphate consists of

						Tupputi.	Mitscherlich.		R Phillips.				
									<i>square prism.</i>	<i>rhombic p.</i>			
Oxide of nickel	1	. .	36	. .	25.9	. .	25.63	} 54.4	. .	26.2	. .	26.30	
Sulphuric acid	1	. .	40	. .	28.8	. .	29.37		. .	30.0	. .	28.16	
Water	. . .	7	. .	63	. .	45.3	. .	45.00	45.6	. .	43.8	. .	45.54
	<u>1</u>		<u>139</u>		<u>100.0</u>		<u>100.00</u>	<u>100.0</u>	<u>100.0</u>		<u>100.0</u>		<u>100.00</u>

SULPHATE OF AMMONIA AND NICKEL is formed by evaporating a mixed solution of sulphate of ammonia and sulphate of nickel; it forms four-sided prismatic crystals, of a green colour, soluble in 4 parts of cold water, and consisting, according to Mitscherlich, of 1 atom of sulphate of ammonia, 1 of sulphate of nickel, and 8 water.

SULPHATE OF POTASSA AND NICKEL is obtained by adding potassa to sulphate of nickel (not in excess), filtering and evaporating; or by mixing and evaporating the solution of sulphate of nickel, and sulphate of potassa. It forms green rhomboidal crystals, (Brooke, *Ann. of Phil.*, vi., 438,) of a sweetish and bitter taste, soluble in 9 parts of cold water (Tupputi, *Ann. de Chim.*, lxxviii. and lxxix.) It has been analyzed by Mitscherlich, and by Cooper (*Ann. of Phil.*, vi., 440), and consists of

						Mitscherlich.	Cooper.			
Potassa	. . .	1	. .	48	. .	22.0	. .	21.58	. .	20.48
Oxide of nickel	. .	1	. .	36	. .	16.5	. .	17.10	. .	17.54
Sulphuric acid	. .	2	. .	80	. .	36.7	. .	36.63	. .	37.90
Water	. . .	6	. .	54	. .	24.8	. .	24.69	. .	24.08
	<u>1</u>		<u>218</u>		<u>100.0</u>		<u>100.00</u>		<u>100.00</u>	

SULPHATE OF NICKEL AND IRON is formed by dissolving the mixed protoxides in sulphuric acid. It is a green efflorescent salt, in tabular crystals.

PHOSPHURET OF NICKEL is a brittle whitish compound, decomposed by exposure to heat and air. It is formed by the action of phosphorus upon red-hot nickel, and is more fusible than the pure metal. It contains, according to Pelletier, 83 nickel + 17 phosphorus; according to Lampadius, 87 nickel + 13 phosphorus.

HYPOPHOSPHITE and PHOSPHITE OF NICKEL remain unexamined.

PHOSPHATE OF NICKEL, being nearly insoluble, is precipitated upon adding phosphate of soda to a solution of nickel. It is of a pale-green colour. Digested in phosphate of ammonia, a triple ammonio-phosphate of nickel is formed: it is insoluble in water.

CARBURET OF NICKEL occasionally remains in the form of a shining powder, when a button of the metal, which has long been fused in the contact of carbon, is dissolved in nitric acid. (Ross and Irving, *Ann. of Phil.*, ii.)

CARBONATE OF NICKEL is precipitated in the form of a green powder, when carbonate of potassa is added to sulphate of nickel. When long washed with boiling-water it becomes nearly black. Dried in the air at the temperature of  $60^{\circ}$ , it retains, according to Thomson, 3 proportionals of water. It dissolves in excess of carbonic acid.

AMMONIO-CARBONATE OF NICKEL is a very soluble and difficultly-crystallizable salt. If its solution be heated, carbonic acid and ammonia are evolved, and hydrated oxide of nickel is thrown down.

BORATE OF NICKEL is a pale-green insoluble compound.

CYANURET OF NICKEL is thrown down when a soluble cyanuret is added to a solution of nickel; or when hydrocyanic acid is mixed with acetate of nickel. A *potasso-cyanuret of nickel* is formed when moist cyanuret of nickel is dissolved in cyanuret of potassium: it yields on evaporation yellow rhombic prisms. Similar double cyanurets may be formed with other bases: they were discovered by Wöhler.

FERROCYANURET OF NICKEL is precipitated in the form of a gray or greenish powder when solution of ferrocyanuret of potassium is added to the soluble salts of nickel.

ALLOYS OF NICKEL. Of these alloys, there is one which requires particular notice, namely, that with *iron*, which forms the principal metallic ingredient in *aërolites*, or *meteoric stones*. Though we really know nothing of the source or origin of these bodies, it has been ascertained upon satisfactory evidence, that they are not of terrestrial formation; and, consequently, their visits to the surface of our planet have awakened much speculation, and some experimental research.

In the first place, it deserves to be remarked, that we have evidence of the falling of stony bodies from the atmosphere in various countries, and at very remote periods. Such events have been set down by the most accredited of the early historians.

The first tolerably accurate narration of the fall of a meteoric stone relates to that of Ensisheim, near Basle, upon the Rhine. The account, which is deposited in the church, runs thus: A.D. 1492, Wednesday, November 7, there was a loud clap of thunder, and a child saw a stone fall from heaven: it struck into a field of wheat, and did no harm, but made a hole there. The noise it made was heard at Lucerne, Villing, and other places; on the Monday, King Maximilian ordered the stone to be brought to the castle, and after having conversed about it with the noblemen, said the people of Ensisheim should hang it up in their church, and his Royal Excellency strictly forbade anybody to take anything from it. His Excellency, however, took two pieces himself, and sent another to Duke Sigismund of Austria. This stone weighed 255 lbs.

In 1627, 27th November, the celebrated Gassendi saw a burning stone fall on Mount Vaisir, in Provence: he found it to weigh 59 lbs. In 1672, a stone fell near Verona, weighing 300 lbs. And Lucas, when at Larissa, in 1706, describes the falling of a stone, with a loud hissing noise, and smelling of sulphur. In September, 1753, de Lalande wit-

nessed this extraordinary phenomenon near Pont de Vesle. In 1768, no less than three stones fell in different parts of France. In 1790, there was a shower of stones near Agen, witnessed by M. Darcet, and several other respectable persons. And on the 13th of December, 1795, a stone fell near Major Topham's house, in Yorkshire; it was seen by a ploughman and two other persons, who immediately dug it out of the hole it had buried itself in; it weighed 56 lbs\*. We have various other and equally satisfactory accounts of the same kind. All concur in describing a luminous meteor, moving through the air in a more or less oblique direction, attended by a hissing noise, and the fall of stony or semi-metallic masses, in a heated state. We have, however, evidence of another kind, amply proving the peculiar origin of these bodies. It is, that although they have fallen in very different countries, and at distant periods, when submitted to chemical analysis, they all agree in component parts; the metallic particles being composed chiefly of nickel and iron; the earthy of silica and magnesia.

Large masses of *native iron* have been found in different parts of the world, of the history and origin of which nothing very accurate is known. Such are the great block of iron formerly at Elbogen, in Bohemia; the large mass discovered by Pallas, weighing 1600 lbs., near Krasnorjark, in Siberia; that found by Goldberry, in the great desert of Zahra, in Africa; probably, also, that mentioned by Mr. Barrow, on the banks of the great fish-river in Southern Africa; and those noticed by Celis, Humboldt, and others in America, of enormous magnitude, some exceeding 30 tons in weight. That these should be of the same source as the other meteoric stones, seems at first to startle belief; but when they are submitted to analysis, and the iron they contain found alloyed with nickel, it no longer seems credulous to regard them as of meteoric origin. We find nothing of the kind in the earth. Two blocks of such iron were, in fact, observed to fall from a meteor, at Hradschina, near Agram, in Croatia, in 1751.

To account for these uncommon visitations of metallic and lapideous bodies, a variety of hypotheses have been suggested.

Are they merely earthy matter, fused by lightning? Are they the offspring of any terrestrial volcano? These were once favourite notions; but we know of no instance in which similar bodies have in that way been produced, nor do the lavas of known volcanos in the least resemble these bodies; to say nothing of the inexplicable projectile force that would here be wanted. Those who have taken up this conjecture, have assumed one impossibility to account for what they conceive to be another, namely, that the stony bodies should come from any other source than our own globe.

The notion that these bodies come from the moon, is, when impartially considered, neither absurd nor impossible, for any power which would move a body 6000 feet in a second, that is, about three times the velocity of a cannon-ball, would throw it from the sphere of the moon's attraction into that of our earth. The cause of this projective force may be a volcano, and if thus impelled, the body would reach us in about two days,

\* In Ure's *Chemical Dictionary* there is a full chronological list of meteoric stones. (Art. METEOROLITE.) See also *Annals of Philosophy*, N. S., vol. xii., p. 83.

and enter our atmosphere with a velocity of about 25,000 feet in a second. Their ignition may be accounted for, either by supposing the heat generated by their motion in our atmosphere sufficient to ignite them, or by considering them combustible, and ignited by contact of air.

While we are stating the *possibility* of these opinions, it may be remembered, that in the great laboratory of the atmosphere, chemical changes *may* happen, attended by the *production* of metals; that, at all events, such a circumstance is within the range of possible occurrences; and that these meteoric bodies may be formed in the air.

Meteoric stones have generally an uneven black surface, and are internally of a gray colour and coarse texture. When carefully examined, most of them appear made up of a number of small spherical bodies and metallic grains imbedded in a softer matter, composed, according to Mr. Howard (*Phil. Trans.*, 1802), of silica, magnesia, and iron with a little nickel; the spherical bodies are nearly of similar composition; and the metallic grains are partly *meteoric iron*, and partly the same with a little sulphur. In addition to these substances, Vauquelin found 2 *per cent.* of chrome in a stone which fell at Langres, in 1815. (*Ann. de Chim. et Phys.*, i. 53.) And Stromeyer detected cobalt in the meteoric iron from the Cape of Good Hope. (Thomson's *Annals*, ix.) Lime and alumine have also been found in them, and a small proportion of manganese. M. Laugier has announced the existence of a meteoric stone without nickel, but containing chrome; and as he has detected the latter metal in all the aërolites which he has examined, he considers it as their most characteristic ingredient. (*Mém. du Muséum*, vi., p. 233.)

In meteoric iron the proportion of nickel varies considerably. In a specimen from the Arctic region I found 3.2 *per cent.* (*Quart. Jour.*, vi., 369.) In that from Siberia, Mr. Children found nearly 10 *per cent.* The analysis may be performed by solution in nitro-muriatic acid; the iron is thrown down by excess of ammonia in the state of peroxide; it is separated by filtration, washed and dried; and on evaporating the filtrated liquor and heating its dry residue red-hot, the oxide of nickel is obtained, which should be redissolved in nitric acid, and precipitated by pure potassa, the mixture being boiled for a few seconds. (Children, *Quart. Jour.*, ix., 324.)

Meteoric iron has been imitated by fusing iron with nickel. The alloy of 90 iron with 10 nickel is of a whitish-yellow cast, and not so malleable as pure iron. The alloy with 3 *per cent.* of nickel is perfectly malleable, and whiter than iron. These alloys are less disposed to rust than pure iron, but nickel alloyed with steel increases the tendency to rust. (Stodart and Faraday, *Quart. Jour. of Science and Arts*, ix.)

Nothing is known of the alloys of nickel with potassium, sodium, manganese, zinc, or tin. With copper it forms a hard white alloy; the *white copper* of the Chinese, or *Pakfong*, which consists, according to the analysis of Dr. Fyfe, of 40.4 parts of copper, 31.6 of nickel, 25.4 of zinc, and 2.6 of iron. A similar alloy is often used as a substitute for silver, or for plated articles, under the name of *German silver*: it should consist of 1 part of nickel, 1 of zinc, and 2 of copper; or, when intended for *rolling*, of 25 parts of nickel, 20 of zinc, and 60 of copper; to which, if for *casting*, 3 of lead may be added. (Gersdorff, *Quarterly Journal*, i.,

1827, 483.)\* Nickel and arsenic have a strong mutual attraction; hence arsenic cannot be expelled from nickel by heat. A small addition of arsenic renders nickel more fusible, and does not destroy its magnetic power. The ores of nickel, called *kupfernickel* and *glance-nickel*, are *native arsenurets*.

CHARACTERS OF THE SALTS OF NICKEL. These salts have a rough metallic taste, and excite vomiting when swallowed in sufficient quantity. They are recognised by the peculiar green colour of their aqueous solutions, by the green precipitate which they afford with the fixed alkalis and their carbonates, and by giving a green precipitate with ammonia, soluble in excess of that alkali, when it assumes a blue colour. The yellow-green precipitate afforded by iodide of potassium, is very characteristic of nickel; but the nicest test of its presence is the ferrocyanuret of potassium, which produces a pale-gray or greenish-white precipitate in all the solutions of the metal. To detect the presence of nickel in iron, Dr. Wollaston recommends that a small portion, which need not exceed .01 of a grain, should be filed from the sample, and dissolved in a drop of nitric acid; evaporate this to dryness, and add a drop or two of liquid ammonia, which, when gently warmed, will dissolve any oxide of nickel that may be present. The transparent part of the fluid is then to be conducted by the end of a glass rod to a small distance from the precipitated oxide of iron, and mixed with a drop of the ferrocyanuret, which, if nickel be present, will cause an immediate milkiness, not discernible in a solution of common iron, formed and treated in the same way. Nickel is not precipitated in a metallic form by any metal except iron, which is slow and imperfect in its operation. Zinc, immersed in a solution of chloride of nickel, becomes covered with a suboxide, or a mixture of the metal and its protoxide.

\* Whilst correcting this sheet for the press, Mr. Brayley, of the London Institution, has been good enough to refer me to an essay, containing much useful information on the manufacture of *German Silver*, by Messrs. Topping (London, 1836), from which I make the following extracts, premising that the metals should be as pure as possible:

1. *Common German Silver*.—Copper 8, Nickel 2, Zinc  $3\frac{1}{2}$ .

This is the commonest that can be made, with any regard to the quality of the article produced. It might do for wire, for common purposes. If the quantity of the nickel be reduced much below this, the alloy will be little better than pale brass, and tarnish rapidly.

2. *Good German Silver* — Copper 8, Nickel 3, Zinc  $3\frac{1}{2}$ .

This is a very beautiful compound. It has the appearance of silver a little below standard; by some persons it is even preferred to the more expensive compounds. We strongly recommend manufacturers not to use a metal inferior to this.

3. *Electrum*.—Copper 8, Nickel 4, Zinc  $3\frac{1}{2}$ .

This is the compound we first introduced. We still prefer it to any of the others, and we think the public in general would do the same. It has a shade of blue, like very highly-polished silver: it tarnishes less easily than silver.

4. Copper 8, Nickel 6, Zinc  $3\frac{1}{2}$ .

This is the richest in nickel that can be made, without injuring the mechanical properties of the metal. It is a very beautiful compound, but requires a higher heat for fusion than the preceding, and will be found rather more difficult to work.

5. *Tutenag*.—Copper 8, Nickel 3, Zinc  $6\frac{1}{2}$ .

These proportions we originally obtained by analyzing a piece of Chinese *tutenag*, of the best ordinary quality; but have seen some rare specimens of Chinese *tutenag* equal to *electrum*, No. 3. This alloy is very fusible, but very hard, and not easily rolled: it is best adapted for casting.

*Before the blowpipe* oxide of nickel becomes black at the extremity of the exterior flame, and in the interior greenish-gray. It is dissolved readily, and in large quantity, by microcosmic salt. The glass, while hot, is a dirty dark-red, which becomes paler and yellowish as it cools. After the glass has cooled, it requires a large addition of the oxide to produce a distinct change of colour. It is nearly the same in the exterior and interior flame, being slightly reddish in the latter. Nitre added to the bead makes it froth, and it becomes red-brown at first, and afterwards paler. It is easily fusible with borax, and the colour resembles the preceding. When this glass is long exposed to a high degree of heat in the interior flame, it passes from reddish to blackish and opaque, then blackish-gray, and transparent; then paler reddish-gray, and clearer; and lastly, transparent, and the metal is precipitated in small white metallic globules. The red colour seems here to be produced by the entire fusion or solution of the oxide, the black by incipient reduction, and the gray by the minute metallic particles before they combine and form small globules. When a little soda is added to the glass formed with borax, the reduction is more easily effected, and the metal collects itself into one single globule. When this oxide contains iron, the glass retains its own colour while hot, but assumes that of the iron as it cools.

#### § XV. COPPER.

COPPER, *Cuprum*, or *Venus*, of the alchymists (♀), was known in the early ages of the world, and was the principal ingredient in domestic utensils, and in the instruments of war, previous to the discovery of malleable iron. The word *copper* is derived from the island of *Cyprus*, where it was first wrought by the Greeks. It is found *native*, and in various states of combination. Of its *ores*, the oxide, chloride, sulphuret, sulphate, phosphate, carbonate, and arseniate, are the most remarkable.

The metal may be obtained perfectly pure by dissolving the copper of commerce in nitric acid; the solution is diluted, and a plate of iron is immersed, upon which the copper is precipitated. It may be fused into a button, after having been previously washed in dilute sulphuric acid to separate a little iron that adheres to it.

Copper has a red colour and much brilliancy: it is very malleable and ductile, and has a peculiar smell when warmed or rubbed. It melts at a cherry-red or dull-white heat, or, according to Daniell, at a temperature intermediate between the fusing-points of silver and gold, = 1996° Fahr. Its specific gravity varies from 8.86 to 8.89. Under a flame, urged by oxygen gas, it takes fire, and burns with a beautiful green light. Exposed for a long time to damp air, copper becomes covered with a thin greenish crust of carbonate. If heated and plunged into water, a quantity of reddish scales separate, consisting of an imperfect oxide. The same scales fly off during cooling from a plate of the metal which has been heated red-hot. Copper does not decompose water at a red-heat. The equivalent of copper is 32. (31.6 Turner, 32 Gmelin.)

*Native Copper* occurs in a variety of forms; massive, dendritic, granular, and crystallized in cubes, octoëdra, &c. It is found in Cornwall, Siberia, Saxony, Hanover, Sweden, and America; chiefly, but not exclusively, in primitive rocks.

**COPPER AND OXYGEN.** There is only one salifiable oxide of copper, which, therefore, is generally regarded as the *protoxide*; but there is a *suboxide*, or *dioxide* ( $2Cu + O$ ), which occurs *native*, and which may be formed artificially, not by the direct oxidizement of copper, but by processes in which oxygen is abstracted from the protoxide; thus it may be formed by heating 5 parts of peroxide with 4 of very finely divided metallic copper, or by digesting a mixture of 50 parts of finely divided metallic copper, and 58 of peroxide of copper, in 400 of muriatic acid. When potassa is added to this solution, a *hydrated* compound, of an orange-colour, falls; if quickly dried out of the contact of air, it becomes of a red-brown.

When this oxide is intensely heated out of contact of air, it frequently happens that small octoëdral and cubic crystals are formed in it; the same thing was observed by Mr. Chenevix, on exposing peroxide or hydrate of copper to a violent heat, in an open crucible, without addition; a semifused mass, resembling native red copper, was obtained. (*Phil. Trans.*, 1801.) The dilute acids resolve this oxide into metallic copper and peroxide; but it dissolves in concentrated muriatic acid, forming a dark-brown solution. It dissolves in ammonia, as will presently be more fully explained, but it does not dissolve in solutions of potassa or of soda.

This compound may be regarded as consisting of 1 atom of copper and 1 of protoxide; or of

						Chenevix.	Berzelius.		
Copper . . .	2	..	64	..	88.8	..	88.5	..	88.97
Oxygen . . .	1	..	8	..	11.2	..	11.5	..	11.03
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		72		100.0		100.0		100.00

Copper vessels, such as tea-urns &c., and medals, are often superficially coated with this oxide, or *bronzed*; it gives them an agreeable appearance, and prevents tarnish. For this purpose two processes are resorted to:—1. The copper surface is cleaned, and then brushed over with peroxide of iron (generally colcothar) made into a paste with water, or with a very dilute solution of acetate of copper; heat is then cautiously applied in a proper furnace or muffle, till it is found, on brushing off the oxide, that the surface beneath has acquired its proper hue. 2. Two parts of verdigris and one of sal-ammoniac are dissolved in vinegar; the solution is boiled in a pipkin, skimmed, and diluted with water till it only tastes slightly of copper and ceases to deposit a white precipitate; it is then poured into another pipkin or copper-pan, and rapidly brought to boil, and the medal, previously rendered bright, and *perfectly clean*, is dipped into the boiling solution, which may be most conveniently done by placing it in a small perforated copper-ladle or wire-cullender made for the purpose: the surface of the medal becomes at first black or dark-blue, and then (in about 5 minutes) acquires the desired brown tint; it must then be instantly withdrawn, (otherwise it changes colour,) and washed in a stream of water so as perfectly to remove all soluble matters from its surface, and lastly, very carefully dried. The medal is generally perfected by afterwards giving it one gentle pinch between the dies, in the coining-press. When there are

many medals, each must be done separately, as they must not be allowed to touch each other, and care should be taken to rest them upon as few points of contact as possible. The bronzing-liquid also must not be suffered to concentrate by evaporation, but must be diluted if necessary, so as to keep it in a proper state, and especially to avoid all appearance of a white precipitation in it. It is better that the process should be too slowly than too rapidly effected. The pieces must be most carefully washed, and then well dried by wiping with a very soft and warm linen-cloth.

*Native Oxide of Copper*, or *Ruby Copper*, is of a red or steel-gray colour, soft and brittle, and occurs massive, and crystallized in octoëdra, dodecaëdra, and cubes. Its specific gravity is 6. There is a beautiful variety in fine *capillary* crystals; and another, which is compact and earthy, called *Tile Ore*. Cornwall abounds in fine specimens of this ore.

PROTOXIDE OF COPPER ( $Cu + O$ ) or  $Cu$ . When copper is exposed to heat and air, its surface tarnishes, acquiring a yellow and then a violet colour, and at a high temperature black scales form upon it, which are thrown off on plunging it into water, or which fly off as it cools, in consequence of the rapid contraction of the metal. When these scales are heated red-hot so as to ensure perfect oxidizement, they afford a black powder, specific gravity 6.4. Before the blowpipe, this oxide fuses when intensely heated by the tip of the flame, upon charcoal; by the interior of the flame it readily affords a globule of metal. It dissolves in the acids, and is the basis of all the common salts of copper. When alkalis are dropped into its solutions, they throw it down in the form of a bulky blue *hydrate*, which, however, is not permanent at a boiling heat, but becomes black and anhydrous. This oxide of copper is not soluble in the liquid fixed alkalis; but when carbonate of potassa or of soda are fused with it, it expels carbonic acid, and combines to form a blue or green compound. Its combination with ammonia will presently be noticed. It communicates a green, and sometimes a blue tint to vitreous compounds; and Sir H. Davy has shown that it is the basis of certain colours used by the ancients, which have been supposed to contain cobalt. (*Phil. Trans.*, 1815.) It consists of

				Proust.	Berzelius.	Gay Lussac. †
Copper . . .	1	.. 32	.. 80	.. 80	.. 80.13	.. 80.28
Oxygen . . .	1	.. 8	.. 20	.. 20	.. 19.87	.. 19.72
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1	40	100	100	100.00	100.00

This oxide is sometimes considered as a *deutoxide* ( $Cu + 2 O$ ), and the dioxide as a *protoxide*: in this case 64 becomes the equivalent of copper. Gmelin and Berzelius, however, regard the salifiable oxide as the *protoxide*, or as constituted of 1 atom of copper and 1 of oxygen: Turner also has adopted this view, and urges in favour of it, 1. that the general characters of a suboxide belong to the red oxide: 2. that the equivalent of copper deduced from its sp. heat (p. 149) is 32; and 3. that the salts of the black oxide of copper are isomorphous with those of the protoxide of iron; which, he says, gives a strong presumption that those oxides possess the same atomic constitution. To these arguments it may be added that the electrochemical equivalent of copper appears to be 32.



COPPER AND CHLORINE.—Gaseous chlorine acts upon copper with great energy, and produces *two* chlorides; the one a comparatively fixed fusible substance, which is the *dichloride*: the other a volatile yellow substance, which is a *protochloride*.

DICHLORIDE OF COPPER ( $2Cu + C$ ) was first described by Boyle in 1666, under the name of *Rosin of Copper*. It may be obtained by exposing copper-filings to the action of chlorine not in excess: or by evaporating the solution of dioxide of copper in muriatic acid, and heating the residue in a vessel with a very small orifice; or by heating the protochloride in the same way. It is also the residue of the distillation of a mixture of two parts of corrosive sublimate and one of copper-filings. It is insoluble in water, but soluble in muriatic acid, from which potassa throws down the dioxide. When water is added to its muriatic solution, it is thrown down in the form of a white granular hydrate: its colour varies, being generally dark-brown; but if fused and slowly cooled, it is yellow, translucent, and crystalline. It consists of

			J. Davy.
Copper . . . .	2	64	64
Chlorine . . . .	1	36	36
	1	100	100

HYDRATED DICHLORIDE OF COPPER; SUBMURIATE OF COPPER. When moistened dichloride of copper is exposed to air it acquires a greenish white colour, and becomes converted into a compound of chloride and oxide of copper, which has been termed *submuriate of copper*, or *Brunswick green*: the same compound may be formed by adding hydrated oxide of copper to a solution of the muriate; or by exposing to the atmosphere slips of copper partially immersed in muriatic acid. This compound consists, according to John Davy, of 4 atoms of protoxide of copper, 1 of muriatic acid, and 3 of water.

*Native Submuriate of Copper* is found in Peru and Chili, sometimes in the form of green sand, and sometimes massive and crystallized. The *green sand* was found in the river Lipas, in the desert of Atacama, separating Peru from Chili; hence mineralogists have termed this variety *Atacamite*. Muriate of copper has also been found upon some of the lavas of Vesuvius. The primitive form of this substance is an octoëdron. It is of a deep-green colour, and contains, according to Dr. Davy's analysis, 73 oxide of copper, 16.2 muriatic acid, and 10.8 of water.

CHLORIDE OF COPPER ( $Cu + C$ ) may be formed by dissolving protoxide of copper in muriatic acid, and evaporating to dryness by a heat below  $400^{\circ}$ . It is soluble in water, producing a solution, from which potassa precipitates the hydrated protoxide; its colour is yellow, but it becomes white and afterwards green when exposed to heat and moisture. Exposed to a red-heat in a tube with a very small orifice, gaseous chlorine is expelled, and it becomes a dichloride. It readily absorbs ammonia, and forms a blue pulverulent mass. It consists of

			J. Davy.
Copper . . . .	1	32	47
Chlorine . . . .	1	36	53
	1	68	100

**HYDRATED CHLORIDE OF COPPER: MURIATE OF COPPER.** Muriatic acid acts with difficulty on metallic copper, except it be concentrated and boiling; but it readily dissolves the protoxide, forming a brown or grass-green solution, according to its state of dilution. By carefully evaporating and cooling this solution, it crystallizes in prismatic parallelepipeds which are deliquescent, and very soluble in water and alcohol. Mr. Kane has shown the curious fact, that the hydrated chloride or muriate of copper may be obtained by the action of muriatic acid upon crystallized sulphate of copper. (*Phil. Mag. and Ann.*, April, 1836.)

**CHLORATE OF COPPER ( $Cu + C'$ )** is a blue-green deliquescent salt, difficultly crystallizable, formed by dissolving peroxide of copper in chloric acid. A piece of paper dipped into its solution, burns with a remarkable green flame. (Vauquelin.) This salt is formed, according to Chenevix, by passing chlorine through a mixture of oxide of copper and water.

**IODIDE OF COPPER ( $Cu + i$ )** is precipitated from solutions of the metal by hydriodic acid. It is brown and insoluble.

**IODATE OF COPPER. ( $Cu + i'$ )** When solution of iodate of potassa is added to solutions of copper, an insoluble *iodate of copper* is thrown down.

**BROMIDE OF COPPER** has not been examined.

**FLUORIDE OF COPPER.** When hydrated dioxide of copper is added to hydrofluoric acid, and evaporated out of the contact of air, a fusible compound of a black colour, while hot, but becoming red as it cools, is obtained, which is a *difluoride of copper*. It forms a dark solution in hydrofluoric acid, and is precipitated white by water, but becomes red when collected upon a filter. When carbonate of copper is dissolved in hydrofluoric acid, carbonic acid is evolved, and an insoluble compound is at length formed, the properties of which are not very explicitly detailed by Berzelius, who alone has examined this and the preceding compound.

**NITRATE OF COPPER. ( $Cu + n'$ )** Nitric acid, diluted with three parts of water, rapidly oxidizes copper, evolving nitric oxide, and ultimately forming a bright-blue solution, which affords deliquescent prismatic crystals on evaporation, of a fine blue colour, and very caustic. They contain a considerable portion of water, which causes them to liquefy at a temperature below  $212^{\circ}$ . At a higher temperature they lose water and acid, becoming a *subnitrate*, and are entirely decomposed at a red-heat. The anhydrous nitrate of copper consists of

Oxide of copper . . . .	1	..	40	..	42.5
Nitric acid . . . .	1	..	54	..	57.5
	1		94		100.0

The quantity of water contained in the crystallized nitrate has not been satisfactorily determined. Potassa forms, in the solution of this nitrate, a bulky blue precipitate of *hydrated oxide of copper*, which, as already observed, when boiled in potassa or soda, becomes black from the loss of its combined water. When nitrate of copper is coarsely powdered, sprinkled with a little water, and quickly rolled up in a sheet of tin-foil, there is great heat produced, nitrous gas is rapidly evolved, and the metal often takes fire. (Higgins, *Phil. Trans.*, lxiii.) If ammonia be added to solution of nitrate of copper, it occasions a preci-

pitate of the hydrated oxide; but if it be added in excess, the precipitate is redissolved, and a triple *ammonio-nitrate of copper* is produced. It is a soluble crystallizable salt, which detonates slightly when heated.

**SUBNITRATE OF COPPER.** When caustic potassa, not in excess, is added to solution of nitrate of copper, or when the salt is carefully heated so as to expel part of its acid, and the residue washed, there remains an insoluble pale green salt, composed of

					Berzelius.	Proust.
Oxide of copper	5	..	200	..	66.89	.. 66.0
Nitric acid . .	1	..	54	..	18.06	.. 18.9
Water . . .	5	..	45	..	15.05	.. 17
	<u>1</u>		<u>299</u>		<u>100.00</u>	<u>100</u>

**AMMONIURET OF OXIDE OF COPPER; CUPRATE OF AMMONIA.** If oxide of copper be digested in ammonia it is dissolved, forming a bright-blue solution, which, by careful evaporation, affords dark blue crystals. A mixture of lime, sal-ammoniac, and water, placed in a copper vessel, or mixed with oxide of copper, also affords a deep blue liquor in consequence of the action of the ammonia on the oxide of copper. This solution is the *Aqua Sapphirina* of old pharmacy.

The dioxide of copper also dissolves in ammonia, but the solution is colourless; if it be exposed to air it becomes blue. This may be well shown by filling a tall glass with liquid ammonia, and adding a few drops of solution of the dichloride of copper; the liquid presently acquires a blue colour upon the surface, but remains for some time colourless below. If clean copper-filings be digested in a well-stopped phial with liquid ammonia, a colourless solution of the dioxide is also formed, which becomes blue on momentary exposure to air. When these ammoniacal solutions are very copiously diluted, or when potassa is added to them, they are decomposed, and hydrated oxide of copper falls.

**COPPER AND SULPHUR; DISULPHURET OF COPPER, ( $2Cu + S$ ),** may be formed artificially, by heating a mixture of copper-filings and sulphur: as soon as the latter melts, a violent action ensues, the copper becomes red-hot, and a black brittle compound is formed. It may also be produced by fusing sulphur with oxide of copper. It is soluble in muriatic acid, with the evolution of sulphuretted hydrogen; and in nitric acid, with the separation of sulphur. It consists of

					Berzelius.	Vauquelin.
Copper . .	2	..	64	..	80	.. 79.73
Sulphur . .	1	..	16	..	20	.. 20.27
	<u>1</u>		<u>80</u>		<u>100</u>	<u>100.00</u>

*Native Disulphuret of Copper; Vitreous Copper.* This ore of copper is chiefly found in primitive countries. In England, it occurs in great beauty, crystallized and massive, in Cornwall, and in Yorkshire. Its colour is gray; its lustre shining and metallic; and it yields easily to the knife. Its primitive form is a six-sided prism, which passes into the dodecaëdron with triangular faces, and various modifications of it. A variety of *black sulphuret of copper*, containing iron and arsenic, has been described by Messrs. W. and R. Phillips, under the name of *Tennantite*;

its most ordinary form is the rhomboidal dodecaëdron, either perfect or variously modified. (*Quarterly Journal of Science and Arts*, vii., 95.)

**SULPHURET OF COPPER.** ( $Cu + S$ .) This compound cannot be formed by fusion, but it is thrown down when sulphuretted hydrogen is passed through a solution of protoxide of copper: the precipitate is at first brown, but becomes black, and when dried assumes a greenish hue. In this state it reddens moistened litmus paper, and when heated gives off a little water and sulphurous acid, and sulphur, and the disulphuret remains. It is insoluble in potassa, and in the sulphuretted alkalis. It consists of

Copper	.	.	.	1	..	32	..	50
Sulphur	.	.	.	1	..	16	..	50
				1		48		100.

**FERROSULPHURETS OF COPPER.** *Copper Pyrites*, or *Yellow Copper Ore*, is the most important and generally occurring ore, from which the largest proportion of the copper of commerce is derived; it occurs in a variety of forms, its primitive crystal being the regular tetraëdron. The Cornish mines are very productive of this ore, and it is the principal product of the Parys mountain mine in Anglesea. A beautiful iridescent variety occurs in the Ecton mine in Staffordshire. The composition of the different varieties of copper pyrites, appears in all cases to be sulphur, copper, and iron. The *variegated copper* Mr. Phillips regards as a compound of 1 proportional of sulphuret of iron, 2 proportionals of sulphuret of copper. (*Ann. of Phil.*, iii., 87.)

The *yellow copper ore* is also a double sulphuret of iron and copper: and, omitting the small portion of lead and arsenic with which it is usually contaminated, it may be considered as a compound of 2 proportionals of sulphuret of iron, 1 proportional of sulphuret of copper. (Phillips, *Ann. of Phil.*, iii., 301.)

**REDUCTION OF COPPER ORES.** The following is an outline of the process by which these ores of copper are reduced, as carried on upon a very large scale near Swansea, where the chief part of the Cornish ores are brought to the state of metal. The ore, having been picked and broken, is heated in a reverberatory furnace, by which arsenic and sulphur are driven off. It is then transferred to a smaller reverberatory, where it is fused, and the slag which separates, being occasionally removed, is cast into oblong masses used as a substitute for bricks. The impure metal collected at the bottom of the furnace is granulated by letting it run into water; it is afterwards remelted and granulated two or three times successively, in order further to separate impurities, which are chiefly sulphur, iron, and arsenic, and ultimately cast into oblong pieces called *pigs*, which are broken up, roasted, and lastly melted with a portion of charcoal in the refining furnace. Malleability is here conferred upon the copper, and its texture improved, by stirring the metal with a pole of green wood, generally birch, which causes great ebullition and agitation; assays are occasionally taken out, and the metal, originally crystalline and granular when cold, now becomes fine and close, so as to assume a silky polish when the assays are half cut through and broken. The metal is now cast into cakes about 12 inches wide by 18 in length. The whole process

of refining the copper, and toughening it by *poling*, requires much care and attention; and if it be over-poled, the metal is even rendered more brittle than in its original state: the effect of *poling* has not been satisfactorily explained; it may consist in the separation of a small portion of oxide of copper, and the effect of over-*poling* may possibly depend upon the combination of the copper with a portion of carbon. Copper for brass making is granulated by pouring the metal through a perforated ladle into water; when this is warm, the copper assumes a rounded form, and is called *bean-shot*; but if a constant supply of cold water is kept up it becomes ragged, and is called *feathered-shot*. Another form into which copper is cast, chiefly for exports to the East Indies, is in pieces of the length of six inches, and weighing about eight ounces each: the copper is dropped from the moulds, immediately on its becoming solid, into a cistern of cold water, and thus, by a slight oxidation of the metal, the sticks acquire a rich red colour on the surface. This is called *Japan Copper*. A large quantity of copper is rolled into sheets and sheathings, both for export and home consumption. (For an excellent account of the reduction of copper, as carried on in this country, the reader is referred to Mr. Vivian's paper, *Ann. of Phil.*, N.S., v., 113.)

HYPOSULPHITE OF COPPER ( $\text{Cu} + \tilde{\text{S}}$ ) was formed by Herschel by mixing hyposulphite of potassa with sulphate of copper. It is colourless; of an intensely sweet taste; and, provided air be excluded, it is not turned blue by ammonia. (*Edin. Phil. Journ.*, i., 24.)

SULPHITE OF COPPER ( $\text{Cu} + \hat{\text{S}}$ ) may be obtained by passing sulphurous acid into water, through which oxide of copper is diffused. Small red crystals are formed, composed of oxide of copper and sulphurous acid. (Chevreul, *Ann. de Chim.*, lxxxiii., 181.) When sulphite of potassa is added to nitrate of copper a precipitate falls, which assumes the form of red and yellow crystals. The former are sulphite of copper; the latter a triple *sulphite of potassa and copper*. (Chevreul.)

HYPOSULPHATE OF COPPER ( $\text{Cu} + \underline{\text{S}'}$ ) is formed by adding a solution of sulphate of copper to one of hyposulphate of baryta; it crystallizes in small prisms, very soluble in water, but insoluble in alcohol, and slightly efflorescent. When a little ammonia is added to its solution a green powder falls, which is a *subhyposulphate*, composed of 4 atoms of oxide, 1 of acid, and 4 of water. The crystallized neutral hyposulphate contains

	Heeren.				
Oxide of copper . . . . .	1	..	40	.. 27.03	.. 26.43
Hyposulphuric acid . . . . .	1	..	72	.. 48.65	.. 48.10
Water . . . . .	4	..	36	.. 24.32	.. 25.47
	1		148	100.00	100.00

SULPHATE OF COPPER; ROMAN VITRIOL; BLUE VITRIOL ( $\text{Cu} + \text{S}'$ ). This salt is formed by dissolving peroxide of copper in diluted sulphuric acid. It crystallizes in rhomboidal prisms of a fine blue colour, doubly refractive, and soluble in about 4 parts of water at  $60^\circ$ , and in 2 parts at  $212^\circ$ . It may also be formed by boiling copper-filings in sulphuric acid; a process which furnishes abundance of sulphurous acid, but which is not generally had recourse to, to produce sulphate of copper. It is made upon

a large scale, by exposing roasted sulphuret of copper to air and moisture, and thus obtained, is impure, containing iron, and often zinc: it is the common *blue vitriol* of commerce. It is also obtained in large quantities, and very pure, in certain processes afterwards to be described for refining gold and silver; and it is occasionally prepared by dissolving in sulphuric acid a submuriate of copper manufactured for the purpose. When heated, it loses water of crystallization, crumbling down into a white or pale-blue *anhydrous sulphate*, which reabsorbs moisture from the air, so as to reconstitute its crystalline proportion; at a higher temperature sulphuric acid is evolved, unmixed with sulphurous acid, and peroxide of copper remains. It is the *Vitriol*, or *Salt of Venus*, of the alchemists. It is much used in the arts as a source of several blue and green colours. It has also been used to prevent smut in corn, by steeping the grain in a dilute solution of the salt (*Quart. Journ.*, xvi., 156); and minute quantities of it are occasionally added to bread (in Paris especially), to improve its colour and quality (*Archives, Gén. de Médecine*, xxi., 145). In medicine, it is resorted to as a powerful emetic; and, in very minute doses, as a tonic. It is also a valuable external application.

It may be employed to prevent *dry rot* by steeping timber or planks in its solution, and it is a powerful preservative of animal substances, which, when imbued with it, and dried, remain unaltered. The waters of copper-mines often hold it in solution, and, when decomposed by immersing in them pieces of iron, yield precipitated metallic copper. (Copper of cementation.) Anhydrous sulphate of copper consists of

Oxide of Copper . . . . .	1	..	40	..	50	..	Berzelius.	50.9
Sulphuric acid . . . . .	1	..	40	..	50	..		49.1
	<hr/>		<hr/>		<hr/>			<hr/>
	1		80		100			100.0

The crystallized sulphate of copper contains

Oxide of Copper . . . . .	1	..	40	..	32	..	Proust.	32	..	Berzelius.	32.13
Sulphuric Acid . . . . .	1	..	40	..	32	..		33	..		31.57
Water . . . . .	5	..	45	..	36	..		35	..		36.30
	<hr/>		<hr/>		<hr/>			<hr/>			<hr/>
	1		125		100			100			100.00

**TRISULPHATE OF COPPER.** When a solution of sulphate of copper is precipitated by a small addition of potassa, a green, tasteless, insoluble powder falls, composed of

Oxide of Copper . . . . .	3	..	120	..	64.17	..	Berzelius.	64.22
Sulphuric Acid . . . . .	1	..	40	..	21.39	..		21.28
Water . . . . .	3	..	27	..	14.44	..		14.50
	<hr/>		<hr/>		<hr/>			<hr/>
	1		187		100.00			100.00

**AMMONIA-SULPHATE OF COPPER.** When mixed solution of sulphate of copper and sulphate of ammonia is evaporated, blue soluble crystals are obtained, composed of

	Berzelius.				Mitscherlich.						
Ammonia . . . . .	1	..	17	..	8.5	..	1	..	17	..	8.14
Oxide of Copper . . . . .	1	..	40	..	20.0	..	1	..	40	..	19.14
Sulphuric Acid . . . . .	2	..	80	..	40.0	..	2	..	80	..	38.27
Water . . . . .	7	..	63	..	31.8	..	8	..	72	..	34.45
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		200		100.0		1		209		100.00

When a solution of sulphate of copper is supersaturated by ammonia, so as to redissolve the precipitated oxide, dark-blue crystals may be obtained by very careful evaporation, forming the *cuprum ammoniacale* of pharmacy. Exposed to air they lose ammonia, and crumble down in a green powder: (a mixture of sulphate of ammonia and carbonate of copper.) They are soluble in 1.5 cold water, and insoluble in alcohol; the aqueous solution, largely diluted, deposits trisulphate of copper. The crystals consist of

					Berzelius.	Brandes
Ammonia . . . . .	2	34	27.64	26.40	21.42	
Oxide of Copper . . . . .	1	40	32.52	34.00	33.08	
Sulphuric Acid . . . . .	1	40	32.52	32.25	31.75	
Water . . . . .	1	9	7.32	7.35	13.35	
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	
	1	123	100.00	100.00	99.60	

SULPHATE OF COPPER AND POTASSA is a double salt, formed by digesting peroxide of copper in bisulphate of potassa. It crystallizes in rhomboids of a pale-blue colour, and consists of one proportional of sulphate of potassa, one of persulphate of copper, and six of water.

PHOSPHURET OF COPPER (*cu + p*) is most easily made by dropping pieces of phosphorus on red-hot copper-wire. It is more fusible than copper. Its specific gravity is 7.12. Pelletier found it composed of 100 copper + 20 phosphorus.

Neither the *hypophosphite* nor *phosphite of copper* have been examined.

PHOSPHATE OF COPPER. When solutions of sulphate of copper and phosphate of soda are mixed, a bluish-green insoluble powder falls, which is probably a *hydrated subphosphate*, composed, according to Chenevix, (*Phil. Trans.*, 1801,) of 49.5 oxide, 35 acid, 15.5 water.

*Native Phosphate of Copper* has been found near Cologne. It is of a green colour, and forms small rhomboidal crystals. A specimen, analyzed by Mr. Lunn (*Ann. of Phil.*, iii. 182), afforded, phosphoric acid, 21.687, peroxide of copper, 62.847, water, 15.454. It may, therefore, be regarded as a hydrated trisphosphate of copper. ( $3Cu + p' + 3q.$ )

SELENIURET OF COPPER (*cu + se*) is formed by heating copper-filings with selenium: they act with intense ignition, and a black brittle compound results.

SELENITE OF COPPER. When a hot solution of sulphate of copper is mixed with biselenite of ammonia, a precipitate falls, at first yellow, but which afterwards becomes greenish-blue and crystalline. When sulphate of copper is decomposed by selenite of ammonia, with excess of ammonia, a green *diselinite* is precipitated.

CARBURET OF COPPER. The pale yellowish-red and fibrous copper, (overpoled,) appears to contain carbon. (Vivian, *Ann. of Phil.*, v., 121.)

CARBONATES OF COPPER. When hot solutions of copper are precipitated by the carbonated fixed alkalis, a bulky *hydrated dicarbonate of copper*, of a green colour, falls: its tint, when intended for a pigment, is improved by repeated washing with boiling water\*. When native, it is known under the name of *malachite*. It consists of

\* This substance is generally sold in the shops under the name of *mineral green*, or *green verditer*.

	Native						Artificial.	
	Phillips.	Klaproth.	Vauquelin.	Berzelius	Proust.			
Oxide of Copper	2	80	72.07	72.2	70.5	70.00	71.70	69.5
Carbonic Acid	1	22	19.82	18.5	18.0	21.25	19.73	25.0
Water	1	9	8.11	9.3	11.5	8.75	8.57	5.5
	1	111	100.00	100.0	100.0	100.00	100.00	100.0

When it is long boiled in water, or when carefully heated, it becomes of a deep-brown colour, and *anhydrous*, consisting, in that state, which occurs *native*, of

					Thomson.
Oxide of Copper	2	80	78.43	78.42	
Carbonic Acid	1	22	21.57	21.58	
	1	102	100.00	100.00	

When a cold dilute solution of sulphate of copper is decomposed by carbonate of potassa, a blue precipitate falls, which, by careful management during drying, retains its blue colour, and is known in commerce under the name of *blue verditer*\*. It generally contains a little lime. (Phillips, *Quart. Jour.*, iv. 277.) It differs from the green carbonate, according to Colin and Tallefert, (*Ann. de Chim. et Phys.*, xii., 62,) in containing more water. It appears to be a compound of

	Phillips.		Klaproth.		Vauquelin		Pelletier.	
	Native.	Artificial.	Native.	Native.	Artificial.	Artificial.	Artificial.	
Oxide of Copper	3	120	69.37	69.08	67.6	70	68.75	59.7
Carbonic Acid	2	44	25.43	25.46	24.1	24	25.00	30.0
Water	1	9	5.20	5.46	5.9	6	6.25	3.3
Impurities					2.4			7.0

**NATIVE CARBONATES OF COPPER.** *Malachite*, or the *green hydrous carbonate*, is found in various forms, but never regularly crystallized, the octoëdral variety being a pseudo-crystal derived from the decomposition of the red oxide. This mineral occurs in the greatest beauty in the Uralian mountains of Siberia; it is rarely found in Cornwall. It is of various shades of green, and often cut into small slabs, or used as beads and brooch-stones. The pulverulent variety has been termed *chrysocola* and *mountain-green*. The *blue carbonate* is found in great perfection at Chessy, near Lyons; also in Bohemia, Saxony, &c. It occurs crystallized in rhomboids and imperfect octoëdra; it also is found in small globular masses; massive, and earthy. The earthy variety is sometimes called *copper-azure* or *mountain-blue*. The *Diopase* or *Copper Emerald* is a very rare mineral, hitherto found only in Siberia, associated with malachite. It consists, according to Lowitz, of oxide of copper, silica, and water.

**BORATE OF COPPER.** Solution of borax, poured into sulphate of copper, produces a bulky pale-green precipitate of *borate of copper*.

\* There is a very inferior pigment, also called *verditer*, which is a mixture of subsulphate of copper and chalk. According to Pelletier, a good verditer may be obtained as follows: Add a sufficient quantity of lime to nitrate of copper to throw down the hydrated oxide; it gives a greenish precipitate that is to be washed and nearly dried upon a strainer; then incorporate with it from 8 to 10 per cent. of fresh lime, which will give it a blue colour, and dry it carefully. According to Mr. Chenevix, the alkaline carbonates dissolve a portion of the peroxide of copper, and form triple salts.



DICYANURET OF COPPER ( $2Cu + Cy$ ). Hydrocyanic acid and hydrocyanate of potassa throw down a white curdy precipitate, in the solution of dichloride of copper. A similar compound is obtained by the action of dilute hydrocyanic acid upon hydrated dioxide of copper: it is soluble in ammonia, and the solution is colourless; it is also soluble in muriatic acid, and precipitated by dilution, and by potassa: it combines with other metallic cyanurets, forming a class of *cuprocyanurets*.

CYANURET OF COPPER ( $Cu + Cy$ ) is formed by digesting hydrated oxide or carbonate of copper, in dilute hydrocyanic acid: it is a yellow powder, insoluble in water, soluble in muriatic acid, and again precipitable by dilution.

CUPROCYANURET OF POTASSIUM. Cyanuret of copper, digested in a solution of cyanuret of potassium yields a yellow solution, from which small yellow transparent prismatic crystals may be obtained, of a bitter metallic taste. This salt is not altered by the alkalis, but acids precipitate cyanuret of copper from it, which excess of acid afterwards dissolves with the evolution of hydrocyanic acid. (Ittner.) According to L. Gmelin (*Handbuch*, Art. KUPFER) these crystals, if obtained from *oxide* (and not from dioxide) of copper, are a *cupro dicyanuret* of potassium; for during the solution of oxide of copper in cyanuret of potassium, cyanogen is evolved, and the solution yields a white curdy precipitate of dicyanuret of copper on the addition of muriatic acid. When a solution of this cuprocyanuret is added to other metallic solutions, an interchange ensues between the potassium and the metal in the solution, and double cyanurets are formed, in which one of the metals is always copper: the precipitate with *gold* is green; with *silver*, dark-brown; with protosalts of *iron*, greenish-yellow; with the persalts of iron the precipitate is only a mixture of cyanuret of copper with peroxide of iron; with *lead*, pale-green; with *zinc*, *bismuth*, and *manganese*, pale-yellow. Acids decompose these precipitates, dissolving them, and evolving hydrocyanic acid; the compound with iron yields protocyanuret of iron, which becomes blue by exposure to air. All the salts of *tin* yield mere mixtures of cyanuret of copper and oxide of tin: the relative proportion of the copper to the other metals, in these compounds, has not been accurately determined. (Berzelius.)

FERROCYANURET OF COPPER is thrown down by ferrocyanuret of potassium, from the solutions of oxide of copper, in the form of a rich-brown powder, which has been used as a pigment: it is partially soluble in ammonia; insoluble in acids; and decomposed by caustic potassa. Cold concentrated sulphuric acid whitens it, but, on the addition of water, it again becomes brown. Ferrocyanuret of potassium is so delicate a test of the salts of copper, that it will distinctly detect one part of that metal in 60,000 of the solution.

DISULPHOCYANURET OF COPPER is formed by digesting hydrated protoxide of copper with sulphocyanuret of potassium, in acidulated water: the compound is white, insoluble in water and in acids, and very combustible: caustic alkali separates hydrated protoxide from it.

SULPHOCYANURET OF COPPER yields a green solution with water; it is decomposed by many deoxidizing agents, which precipitate the disulphocyanuret, and evolve free sulphocyanic acid.

ALLOYS OF COPPER. Many of the alloys of copper are important. With *gold* it forms a fine yellow ductile compound, used for coin and ornamental work. *Sterling* or *standard gold* consists of 11 gold + 1 copper. The specific gravity of this alloy is 17.157. With *silver* it forms a white compound, used for plate and coin. (See *Gold* and *Silver*, &c.) *Lead* and *copper* require a high red-heat for union; the alloy is gray and brittle. Of the alloys of copper with the preceding metals the most important are *brass* and *bell-metal*. It forms white compounds with *potassium* and *sodium*; a reddish alloy with *manganese*; and a gray one with *iron*.

*Brass* is an alloy of copper and *zinc*. The metals are usually united by mixing granulated copper with calamine and charcoal: the mixture is exposed to heat sufficient to reduce the calamine and melt the alloy, which is then cast into plates. The relative proportions of the two metals vary in the different kinds of brass; there is usually from 12 to 18 *per cent.* of zinc. Brass is very malleable and ductile when cold; and its colour and little liability to rust recommend it in preference to copper for many purposes of the arts: its specific gravity varies from 7.8 to 8.4. According to Sage, a very beautiful brass may be made by mixing 50 parts of oxide of copper, 100 of calamine, 400 of black flux, and 30 of charcoal-powder; melt these in a crucible till the blue flame is no longer seen round the cover; and, when cold, a button of brass is found at the bottom, of a golden colour, and weighing one-sixth more than the pure copper obtained from the above quantity of oxide.

The *analysis of brass* may be performed by solution in nitric acid; add considerable excess of solution of potassa, and boil, which will dissolve the oxide of zinc and leave that of copper; wash the latter, and dry and heat it to redness: 100 parts indicate 80 of copper. The zinc in the filtered alkaline solution may be precipitated by carbonate of soda, having previously added a small excess of muriatic acid; wash this precipitate, dry it, and expose it to a red-heat; it is then oxide of zinc, 100 parts of which indicate 80 of metal. But as, in this process, the whole of the oxide of zinc is not easily removed by the alkaline solution, Mr. Keates recommends the following as a preferable operation: Dissolve the brass in dilute nitric acid, evaporate to dryness, and redissolve in excess of dilute sulphuric acid; filter, to separate sulphate of lead, if any be present; dilute the solution, heat it to its boiling-point, and introduce three polished cylinders of iron, each about an inch long and a fourth of an inch diameter; continue the boiling till the solution becomes colourless, and when tested by a clean plate of iron shows no trace of copper. Filter the solution while hot, and wash the precipitated copper first with very dilute sulphuric acid, and afterwards with boiling water; dry it, and fuse it into a button in a crucible covered with charcoal-powder. Boil the filtered solution with the addition of some nitric acid to peroxidize the iron, and nearly neutralize by carbonate of soda; then add excess of ammonia, to throw down the peroxide of iron, which separate by filtration. Add muriatic acid to the filtered ammoniacal solution, evaporate to dryness, and heat in a silver crucible to drive off muriate of ammonia; dissolve the residue in muriatic acid, and precipi-

tate by excess of carbonate of soda; wash, dry, and ignite the precipitate, which reduces it to the state of oxide of zinc.

*Tutenag* is said to be an alloy of copper, zinc, and a little iron; and *Tombac*, *Dutch Gold*, *Similor*, *Prince Rupert's Metal*, and *Pinchbeck*, are alloys containing more copper than exists in brass, and consequently made by fusing various proportions of copper with brass. According to Wiegleb, *Manheim Gold* consists of 3 parts of copper and 1 of zinc. A little tin is sometimes added, which, though it may improve the colour, impairs the malleability of the alloy. An alloy of 576 parts of copper, 59 of tin, and 48 of brass, is equal to brass in hardness, and may be worked with the same facility; it was used by Mr. Bate for the new standard measures, as being less liable than brass to oxidizement. (*Phil. Trans.*, 1826, part ii., p. 9.)

*Speculum Metal* is an alloy of copper and tin, with a little arsenic; about 6 copper, 2 tin, 1 arsenic. On this subject the reader is referred to Mr. Edwards's experiments. (*Nicholson's Journal*, 4to., iii.) Mr. Little recommends 32 parts of best bar copper, 4 of brass pin-wire,  $16\frac{1}{2}$  of tin, and  $1\frac{1}{4}$  of arsenic. He first melts the brass, and adds about its weight of tin; when this is cold, the copper, previously fused with black flux, is added; then the remainder of the tin; and, lastly, the arsenic. This mixture is granulated, and again fused for casting.

*Bell Metal* and *Bronze* are alloys of copper and tin; they are harder and more fusible, but less malleable, than copper; the former consists of 3 parts of copper and 1 of tin; the latter of from 8 to 12 of tin with 100 of copper. A little zinc is added to small shrill bells. Bronze is softened in texture when heated and then suddenly cooled; heating afterwards hardens it: these effects are the reverse of those produced upon steel.

*The analysis of alloys of tin and copper* may be performed by digestion in nitric acid, which dissolves the copper and converts the tin into insoluble peroxide, which, when washed and dried, consists of 78.4 tin + 21.6 oxygen. The cupreous solution may be decomposed by potassa, and the pure peroxide of copper indicates the quantity of that metal, as in the analysis of brass.

*Tinned Copper.* Vessels of copper used for culinary purposes are usually coated with tin, to prevent the food being contaminated with copper. Their interior surface is first cleaned, then rubbed over with sal-ammoniac. The vessel is then heated, a little pitch spread over the surface, and a bit of tin rubbed over it, which instantly unites with and covers the copper.

CHARACTERS OF THE SALTS OF COPPER. The cupreous salts are nearly all soluble in water, and of a blue or green colour. Ammonia produces a compound of a very deep blue, when added in excess to these solutions; hydrosulphuret of ammonia forms a black precipitate. Ferrocyanuret of potassium is also an excellent test of the presence of copper; it produces a brown cloud in solutions containing the minutest portion of the oxide.

*The metallic precipitation of copper* from its solutions is effected by zinc, iron, cadmium, tin, lead, and cobalt, and, under certain circumstances, feebly by bismuth. The copper seldom appears in a clean metallic state,

but is mostly alloyed by the precipitating metal, or mixed with other products. The different salts of copper are in this way differently affected. Nitrate of copper, for instance, is reduced by zinc, lead, cadmium, and tin, but when quite neutral, and out of the contact of air, iron very imperfectly and slowly acts upon it. In a common acid solution of the nitrate a plate of iron becomes immediately covered with copper. Cobalt acts very slowly, and bismuth only when heated in the solution, and then imperfectly. The reduced copper appears with its metallic lustre and peculiar colour only upon cobalt, lead, and iron; with the other metals it forms alloys of a brown or black colour. With tin, the oxide of that metal is also precipitated. Sulphate of copper is reduced by the other metals much in the same way as the nitrate: iron first becomes covered by pure copper, after which the precipitation of a subsalt of iron gives it a brown colour. The action of lead upon solution of sulphate of copper is very feeble; cobalt acts rapidly, and becomes coated with clean copper. The precipitate upon tin is accompanied by sulphate of tin, in the form of a white shining powder, but if air be excluded, protosulphate of tin remains in the solution, with a portion of sulphate of copper: in such cases the whole of the copper is never separated. Chloride of copper is easily decomposed by iron, tin, zinc, cadmium, and cobalt, and slowly by lead, provided the solution be not acid. The ammoniacal solution of oxide of copper is only reduced by zinc, iron, and cadmium, not by tin, lead, or cobalt. Zinc is by far the most effectual precipitant of copper.

Before the *blowpipe* oxide of copper is not altered by the exterior flame, but becomes suboxide in the interior. With both microcosmic salt and borax it forms a yellow-green glass while hot, but which becomes blue-green as it cools. When strongly heated in the interior flame, it loses its colour, and the metal is reduced. If the quantity of oxide be so small that the colour is not perceptible, its presence may be detected by the addition of a little tin, which occasions a reduction of the oxide to suboxide, and produces an opaque red glass. If the oxide has been fused with borax, this colour is longer preserved; but if with microcosmic salt, it soon disappears by a continuance of heat. The copper may also be precipitated upon iron, but the glass must be first saturated with iron. Alkalis or lime promote this precipitation. If the glass, containing copper, be exposed to a smoky flame, the copper is superficially reduced, and the glass covered while hot with an iridescent pellicle, which is not always permanent after cooling. It is very easily reduced by soda. Salts of copper, when heated before the blowpipe, give a fine green flame.

The presence of organic substances in solutions of copper materially interferes in some cases with the action of reagents, and as, in consequence of the use of copper vessels for culinary purposes, the contamination of food by this poisonous metal is not uncommon, it often requires minute attention in judicial inquiries. (See Christison on *Poisons*, Art. COPPER; and Rose's *Analytical Chemistry*, translated by Griffin.) In these cases the suspected articles must be evaporated to dryness, carefully incinerated, and the residue treated by a little nitric acid: in this way a solution of nitrate of copper may be obtained, upon which the ordinary tests will act.

## § XVI. LEAD.

THE natural compounds of this metal are very numerous. The most important is the *sulphuret*, from which the pure metal is chiefly procured. Lead is also found combined with carbonic, sulphuric, phosphoric, arsenic, molybdic, and chromic acids, and with oxygen and chlorine. It seems doubtful whether lead ever occurs *native*, that is, in a pure state. To obtain lead perfectly pure, it may be dissolved in nitric acid; the solution evaporated to dryness; the dry mass redissolved in water and crystallized; these crystals heated strongly with charcoal afford the metal quite pure.

Lead appears to have been known in the earliest ages of the world. Its colour is blueish-white. It is remarkably flexible and soft, and leaves a black streak on paper. It melts at about  $612^{\circ}$ , and, by the united action of heat and air, is readily converted into an oxide. Its specific gravity is 11.4. At common temperatures and in its ordinary state it undergoes little change by mere exposure to air, and is generally but slowly acted on by the joint agency of air and water; but when in a state of very fine division, as it is obtained diffused through charcoal, by exposing *tartrate of lead* to a red-heat in close vessels, it takes fire when brought into the contact of air. In distilled water, free from air, and in close vessels, a clean surface of lead remains bright; but, under the same circumstances, in open vessels, it soon tarnishes, small crystalline scales of oxide of lead are formed, a portion of which dissolves in the water, and is again slowly precipitated in the form of carbonate. A very minute trace of sulphuric acid, or of a soluble sulphate, in the water, entirely prevents this corrosive effect, and hence it is that common spring-water is kept with considerable impunity in leaden cisterns\*. But this point ought always to be cautiously inquired and examined into, as very deleterious effects have occasionally arisen from the poisonous property of lead, held in solution by water. The means of detecting it are fortunately simple and delicate, as will appear from the details we are about to give: an excellent and useful epitome of all that relates to the action of water on lead, will be found in Dr. Christison's *Treatise on Poisons*, (Art. LEAD.) Exposed upon ignited charcoal to a current of oxygen gas, lead boils and burns with a blue flame, throwing off dense yellow fumes of oxide. It does not decompose water, at any temperature. The alchemists gave this metal the symbol and name of *Saturn*,  $\text{h}_2$ . The equivalent of lead is 104. (104, Gmelin; 103.6, Turner.)

OXIDES OF LEAD. There are four oxides of lead, but the *protoxide* only is a salifiable base.

PROTOXIDE OF LEAD. (*pl* + *o*.) This oxide, which is often known under the name of *Massicot*, may be obtained by exposing the gray powder which gradually forms upon the surface of melted lead, to the further action of heat and air. It is also formed by exposing pure

\* The cisterns should have *wooden* and not leaden covers; in the latter case, the vapour of the water below condenses upon the cover, and often tends to its rapid corrosion, it being in fact distilled water, and not therefore prevented in its action by any saline matters.

nitrate, or subnitrate, or carbonate of lead, to a dull red-heat. When a solution of nitrate of lead is decomposed by an alkali, the white powder which falls is apparently a hydrated oxide. When the protoxide is heated it has a red colour, but in its ordinary state it is lemon or orange yellow, according to the mode in which it has been prepared. At a high red-heat it fuses, and forms, on cooling, a lamellar vitreous mass of a reddish-brown colour: this is often obtained in scales, under the name of *Litharge*: according to Berzelius, it absorbs carbonic acid slowly from the air, and gradually acquires the property of dissolving in acids with effervescence. Protoxide of lead is soluble in potassa and soda, forming yellow liquids, which on evaporation deposit crystalline scales; it also dissolves in baryta, and sparingly in lime-water: this solution has been recommended as a black stain for the hair. When fused with the earths and metallic oxides, it forms vitreous and fusible compounds, hence its use in the manufacture of glass; hence also the readiness with which it corrodes common crucibles when it is kept for a sufficient time in fusion in them. Heated with charcoal, this oxide is easily reduced to the state of metal; it is also reduced, when heated in hydrogen gas. It consists of

		Döbereiner.		Vauquelin.		J. Davy.		Proust.		Richter.	
Lead	1	.	104	.	92.857	.	93.02	.	93	.	92.85
Oxygen	1	.	8	.	7.143	.	6.98	.	7	.	7.15
			<u>112</u>		<u>100.000</u>		<u>100.00</u>		<u>100</u>		<u>100.00</u>

DEUTOXIDE OF LEAD: BINOXIDE OF LEAD: SESQUIOXIDE OF LEAD: RED-LEAD: MINIUM. This substance, which is well known as a common red pigment, is made by exposing protoxide of lead to the action of heat and air, so as to oxidize, without fusing it; it gradually acquires a fine red-colour, the brilliancy of which goes off by exposure to light. To obtain it of a brilliant colour it requires to be made in large quantities and with several precautions. The method formerly employed in Derbyshire is described in Watson's *Chemical Essays*. This oxide is not salifiable, but the acids convert it into protoxide and peroxide; they combine with the former, and leave the latter in the form of an insoluble brown powder. Minium, upon the strength of the following analyses, has generally been regarded as a *sesquioxide*, but, according to Dumas, it is of variable composition. (*Ann. de Chim. et Phys.*, xlix., 398.)

		Berzelius.		Vauquelin.		Richter.						
Lead	. . .	1	. . .	104	. . .	89.66	. . .	90	. . .	91	. . .	83.34
Oxygen	. . .	1½	. . .	12	. . .	10.34	. . .	10	. . .	9	. . .	16.66
		<u>1</u>		<u>116</u>		<u>100.00</u>		<u>100</u>		<u>100</u>		<u>100.00</u>

PEROXIDE OF LEAD ( $pl + 2o$ ) is obtained in the form of an insoluble brown powder by digesting minium in nitric acid, or by passing chlorine through minium diffused in water, or through a solution of acetate of lead, and thoroughly washing the product in hot water to remove the chloride of lead. At a red-heat it gives off oxygen, and is converted into protoxide. Digested in liquid ammonia, a mutual decomposition takes place, and water and nitrate of lead are formed. Triturated with a fifth of its weight of sulphur, it inflames spontaneously. With muriatic acid, it

furnishes chlorine and chloride of lead. It readily absorbs sulphurous acid, and forms with it sulphate of lead. According to Vogel, it becomes red-hot when acted upon by pure sulphurous acid gas. It consists of

						Berzelius.
Lead . . .	1	..	104	..	86.66	.. 86.51
Oxygen . .	2	..	16	..	13.34	.. 13.49
	1		120		100.00	100.00

DIOXIDE OF LEAD. ( $2pl + o.$ ) When *oxalate of lead* is heated to dull-redness in a small retort, carbonic oxide and carbonic acid are evolved, and a dark-gray powder remains, which is resolved by acids into protoxide and metallic lead, and which, according to Dulong, is a definite suboxide. The gray powder with which lead that has been long exposed to air, especially if heated, becomes covered, is, according to Berzelius, similar in composition. Boussingault finds that mercury, triturated under water with this oxide, abstracts no lead from it, and therefore infers that it is not a mixture of metallic lead with the protoxide, notwithstanding its resolution into such a mixture by sulphuric, muriatic, and acetic acids, (*Ann. de Chim. et Phys.*, liv., 264), but that it consists of

Lead . . .	2	..	208	..	96.5
Oxygen . .	1	..	8	..	3.5
	1		216		100.0

CHLORIDE OF LEAD. ( $pl + c.$ ) When laminated lead is heated in chlorine, the gas is absorbed, and a *chloride of lead* results. (J. Davy, *Phil. Trans.*, 1812.) The same substance is obtained by adding muriatic acid to nitrate of lead; it is white and fusible, and, on cooling, forms a hornlike substance (*plumbum corneum*) of the specific gravity of 5.13. It does not absorb ammonia. (Faraday.) It volatilizes at a high temperature provided air has access, in which case a portion of oxide of lead is formed. It dissolves in 30 parts of water at 60°, and in 22 at 212°, separating, as its solution cools, in small anhydrous acicular crystals, unchanged by exposure to air, and of a sweetish taste. It dissolves in dilute nitric acid; it is insoluble in alcohol. A compound of chloride and oxide of lead is sometimes prepared by acting upon a solution of common salt by litharge; solution of soda, and oxide and chloride of lead are formed; this insoluble residue, when fused, is known under the name of *patent-yellow*; when treated by nitric acid, it forms nitrate of lead, and a portion of chloride separates. A similar compound may be obtained by fusing together 1 part of chloride with 4 or 5 of oxide of lead, or by heating 1 part of sal-ammoniac with 10 of oxide of lead. Chloride of lead consists of

					J. Davy.	Döbereiner.
Lead . . . .	1	..	104	..	74.3	.. 75.758
Chlorine . . .	1	..	36	..	25.7	.. 24.242
	1		140		100.0	100.000

*Native Chloride of Lead* has been found amongst the volcanic products of Vesuvius, in small acicular crystals: it has also been found in the Mendip-hills, in Somersetshire: the latter mineral appears, from the analysis of Berzelius, to be a *dichloride*. ( $2pl + c.$ )

CHLORATE OF LEAD ( $Pl + c'$ ) is obtained by digesting the protoxide in chloric acid; it separates by slow evaporation, in white crystalline flakes of a very sweet taste. When heated, it gives out oxygen, and becomes a chloride.

IODIDE OF LEAD, ( $pl + i$ ), formed by heating leaf-lead with iodine, is a yellow compound. It is also formed by adding hydriodic acid or hydriodate of potassa to solution of nitrate of lead; it then falls in the form of a bright-yellow powder, sparingly soluble in boiling water, and separating, as the solution cools, in beautiful brilliant flakes. It is soluble in caustic potassa.

IODATE OF LEAD ( $Pl + i'$ ) is thrown down in the form of a white powder on adding iodate of potassa to any of the soluble salts of lead. It redissolves in excess of the acid. (Pleischl.)

BROMIDE OF LEAD ( $pl + b$ ) is precipitated from a solution of lead by hydrobromic acid; it is fusible, and concretes on cooling into a yellow mass. When first precipitated, it is decomposed by sulphuric and nitric acids; but when fused, it requires boiling sulphuric acid to produce that effect.

BROMATE OF LEAD ( $Pl + b'$ ) is thrown down in the form of a white powder, by adding bromic acid to a dilute solution of nitrate of lead.

FLUORIDE OF LEAD ( $pl + f$ ) is almost insoluble, and obtained by adding hydrofluoric acid to nitrate of lead, when it falls in the form of a white powder, soluble in nitric and muriatic acids, by which, when evaporated, it is decomposed. Ammonia converts the fluoride into a *subfluoride* of lead, which is more soluble than the former.

NITRATE OF LEAD ( $Pl + n'$ ) is obtained by dissolving the metal, not in excess, in dilute nitric acid, and evaporation. It crystallizes in tetraëdra and octoëdra, which have a specific gravity = 4; they are white, anhydrous, translucent, harder than alum, and of a styptic taste; they decrepitate when heated, and when distilled give out nitrous acid vapour and oxygen, and protoxide of lead remains in the retort: they are soluble in 8 parts of water at  $212^{\circ}$ , and insoluble in alcohol. The alkalis throw down a white hydrated protoxide of lead from the solution of this salt, the proportion of water contained in which has not been determined. This salt is of much use in analytical chemistry as a test of the presence of free and combined sulphuric acid (except in *alkaline* solutions, which should be first neutralized with nitric acid). The precipitate is insoluble in nitric acid. Carbonic acid, and the alkaline carbonates, phosphates, oxalates, and tartrates, precipitate nitrate of lead, but the precipitates are soluble in nitric acid. The iodides and bromides, and the chlorides when not very dilute, also precipitate the nitrate of lead: all these precipitates are *white*, with the exception of those by the soluble iodides, which are *yellow*. With sulphuretted hydrogen this solution of lead forms a dark-brown or black precipitate. Nitrate of lead consists of

				Döbereiner.	Chevreul.
Oxide of lead . . .	1 . .	112 . .	67.47 . .	67.6 . .	67
Nitric acid . . .	1 . .	54 . .	32.53 . .	32.4 . .	33
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1	166	100.00	100.0	100



DINITRATE OF LEAD ( $2\text{Pl} + n'$ ) may be formed by boiling a mixture of equal weights of nitrate and protoxide of lead in water, filtering while hot, and setting it by to crystallize; it forms pearly crystals, of a sweet astringent taste, very sparingly soluble in cold water. (Chevreul, *Ann. de Chim.*, lxxxii.) This salt is precipitated, according to Berzelius, by adding ammonia, not in excess, to nitrate of lead: it consists of

		Chevreul.	Berzelius.
Oxide of lead . . .	2 . . . 224 . . . 80.58 . . .	80.14 . . .	80.5
Nitric acid . . .	1 . . . 54 . . . 19.42 . . .	19.86 . . .	19.5
	<hr style="width: 100%; border: 0.5px solid black; margin: 0;"/> 1 . . . 278 . . . 100.00 . . .	<hr style="width: 100%; border: 0.5px solid black; margin: 0;"/> 100.00 . . .	<hr style="width: 100%; border: 0.5px solid black; margin: 0;"/> 100.0

NITRITE OF LEAD. Chevreul and Berzelius have described three *nitrites* of lead, but their composition appears doubtful, and they are regarded by Gmelin as *hyponitrites*. They are obtained by boiling nitrate of lead with metallic lead. A detailed account of them is given by Berzelius. (*Lehrbuch*, ii.)

SULPHURET OF LEAD ( $pl + S$ ) may be formed artificially by fusion. Its lustre and colour much resemble pure lead, but it is brittle, and requires a white-heat for fusion; its sp. gr. is 7.58. Boiled with muriatic acid, chloride of lead and sulphuretted hydrogen are formed; with nitric acid it is converted into sulphate of lead. Sulphuret of lead may be obtained in the humid way, by precipitating any salt of lead by sulphuretted hydrogen; the precipitate is black, or brown if the solution be very dilute; this is so delicate a test of lead, that, according to Pfaff, a solution containing a hundred-thousandth part of the metal is discoloured by it, provided no excess of acid be present. Sulphuret of lead consists of

		Proust.	Vauquelin.	Wenzel.	J. Davy.
Lead . . .	1 . . . 104 . . . 86.66 . . .	86 . . .	86.23 . . .	86.8 . . .	86.9
Sulphur . . .	1 . . . 16 . . . 13.34 . . .	14 . . .	13.77 . . .	13.2 . . .	13.1
	<hr style="width: 100%; border: 0.5px solid black; margin: 0;"/> 1 . . . 120 . . . 100.00 . . .	<hr style="width: 100%; border: 0.5px solid black; margin: 0;"/> 100 . . .	<hr style="width: 100%; border: 0.5px solid black; margin: 0;"/> 100.00 . . .	<hr style="width: 100%; border: 0.5px solid black; margin: 0;"/> 100.0 . . .	<hr style="width: 100%; border: 0.5px solid black; margin: 0;"/> 100.0

*Native Sulphuret of Lead, or Galena*, is the principal source of the vast commercial demands of the metal. It occurs massive and crystallized, chiefly in the older secondary rocks. Its primitive form is the cube, of which there are several modifications, and among them the octoëdron. It often contains traces of silver, and sometimes in such quantity as to render it worth separating, which is effected by exposing the roasted sulphuret to the action of heat and air in shallow earthen dishes; the lead becomes oxidized and converted into litharge, while the silver is left pure, in consequence of its power of resisting the influence of heat and air. This process is called *cupellation*. The litharge is afterwards reduced by fusion with charcoal.

The reduction of *galena* upon a large scale is a sufficiently simple process. The picked ore, after having been broken and washed, is roasted in a reverberatory fire, the temperature being such as to soften but not fuse it. During this operation it is raked till the fumes of sulphur are dissipated, when it is brought into perfect fusion; the lead, reduced by the fuel, sinks to the bottom, and is run out into oblong moulds called *pigs*; the scoriæ are again melted, and furnish a portion of less pure metal. The mines of Great Britain afford an annual produce

of about 48,000 tons of smelted lead, of which nearly the whole is obtained from the sulphuret. There is a specular variety of galena, called in Derbyshire *slickensides*; and which, when touched by the miner's pick, often splits asunder with a kind of explosion.

HYPOSULPHITE OF LEAD ( $PL + \underline{S}$ ) is precipitated in the form of a white powder, by adding solution of nitrate of lead to hyposulphite of potassa. At  $212^{\circ}$  it becomes dark-coloured, and at a higher temperature burns like tinder. Distilled in close vessels, it gives out sulphurous acid, and is converted into sulphuret and sulphate of lead. It requires more than 3000 parts of cold water for solution. It is composed of

					Herschel.		
Oxide of lead . . . .	1	..	112	..	70	..	70.30
Hyposulphurous acid . . . .	1	..	48	..	30	..	29.70
	1		160		100		100.00

SULPHITE OF LEAD ( $PL + \underline{S}$ ) may be obtained by digesting yellow oxide of lead in sulphurous acid; or by adding sulphurous acid or sulphite of potassa to nitrate of lead. It is white, insoluble, and tasteless. When heated it loses sulphurous acid. It is converted by nitric acid into sulphate of lead. It disengages sulphurous acid when acted upon by muriatic, and by sulphuric acid. It consists of

					Thomson.	Gay Lussac.			
Oxide of lead . . . .	1	..	112	..	77.77	..	74.5	..	78
Sulphurous acid . . . .	1	..	32	..	22.23	..	25.5	..	22
	1		144		100.00		100.0		100

HYPOSULPHATE OF LEAD ( $PL + \underline{S'}$ ) is formed by digesting carbonate of lead in hyposulphuric acid, filtering, and evaporating. It forms soluble crystals, which, by the action of ammonia, may be so decomposed as to yield two *subhyposulphates*: the crystals contain

					Heeren.		
Oxide of lead . . . .	1	..	112	..	50.91	..	51.04
Hyposulphuric acid . . . .	1	..	72	..	32.73	..	33.01
Water . . . . .	4	..	36	..	16.36	..	15.95
	1		220		100.00		100.00

SULPHATE OF LEAD. ( $PL + \underline{S'}$ ) Cold sulphuric acid has no action upon metallic lead; but when the metal is boiled in concentrated sulphuric acid, sulphurous acid is evolved, and a white sulphate of lead is formed. It is so insoluble, that it may be formed by adding dilute sulphuric acid, or an alkaline sulphate, to a solution of nitrate of lead, and hence the application of the soluble salts of lead, especially the nitrate and the acetate, as tests of the presence of sulphuric acid and sulphates. Dr. Thomson found, that after having been dried at a temperature of  $400^{\circ}$ , it might be heated to redness in a platinum crucible without losing weight. Heated on charcoal by the blowpipe, it is decomposed and reduced. Sulphate of lead is not *absolutely* insoluble in water; it is insoluble in alcohol and nearly so in nitric acid; muriatic acid partially decomposes it. It is sparingly soluble in excess of sulphuric acid, and separates from it in small prismatic crystals. It is soluble, when recently precipitated, in the fixed alkaline solutions and their carbonates. Accordingly, if a weak solution of nitrate of lead be

dropped into a solution of carbonate of soda containing sulphate of soda, there is either no immediate precipitate, or if formed, it is redissolved on stirring the liquid. Its acid is expelled by the action of silica and of alumina at a red-heat, hence its decomposition when fused in earthen crucibles. Digested with an acid solution of nitrate of baryta, it yields nitrate of lead and sulphate of baryta. Sulphate of lead consists of

					Klaproth.	Berthier.	Berzelius.				
Oxide of lead . . .	1	..	112	..	73.68	..	73.5	..	73.99	..	73.615
Sulphuric acid . . .	1	..	40	..	26.32	..	26.5	..	26.01	..	26.385
	<u>1</u>		<u>152</u>		<u>100.00</u>		<u>100.0</u>		<u>100.00</u>		<u>100.000</u>

*Native Sulphate of Lead* is found in Anglesea, and in Scotland, crystallized in prisms and in octoëdra.

PHOSPHURET OF LEAD may be formed by dropping phosphorus into melted lead. It is of the colour of lead, and soon tarnishes.

HYPOPHOSPHITE OF LEAD has not been examined.

PHOSPHITE OF LEAD (PL +  $\tilde{p}$ ) was prepared by Berzelius by mixing chloride of lead with phosphite of ammonia. It is white, tasteless, and insoluble, and appears to consist of 1 proportional of oxide of lead + 1 proportional of phosphorous acid.

PHOSPHATE OF LEAD (PL +  $p'$ ) is formed by mixing hot solutions of chloride of lead and phosphate of soda: according to Mitscherlich, the phosphate of soda must be dropped into the solution of lead so as to leave the latter in excess, otherwise a subphosphate of lead falls. It is white; insoluble in water and in acetic acid; soluble in fixed alkaline solutions, and in nitric acid. It is decomposed by sulphuric acid, and by hot muriatic acid. It fuses before the blowpipe, and crystallizes on cooling. It consists of

					Thomson.	Berzelius.	Berthier.				
Oxide of lead . . .	1	..	112	..	75.68	..	75	..	76	..	77.5
Phosphoric acid . . .	1	..	36	..	24.32	..	25	..	24	..	22.5
	<u>1</u>		<u>148</u>		<u>100.00</u>		<u>100</u>		<u>100</u>		<u>100.0</u>

SUBSESQUIPHOSPHATE OF LEAD ( $1\frac{1}{2}$  PL +  $p'$ ) is obtained by digesting the *neutral phosphate* in ammonia, or by precipitating acetate of lead by neutral phosphate of soda: it is white, less fusible than the neutral phosphate of lead, and before the blowpipe yields a mixture of metallic lead with the neutral phosphate; it consists of

						Berzelius.	
Oxide of lead . . .	$1\frac{1}{2}$	..	168	..	82.35	..	82.52
Phosphoric acid . . .	1	..	36	..	17.65	..	17.48
	<u>1</u>		<u>204</u>		<u>100.00</u>		<u>100.00</u>

SESQUIPHOSPHATE OF LEAD (PL +  $1\frac{1}{2}$   $p'$ ) is the white powder which falls when a hot solution of chloride of lead is decomposed by biphosphate of soda. It reddens litmus, and consists of

						Berzelius.	
Oxide of lead . . .	1	..	112	..	67.47	..	69.731
Phosphoric acid . . .	$1\frac{1}{2}$	..	54	..	32.53	..	30.269
	<u>1</u>		<u>166</u>		<u>100.00</u>		<u>100.000</u>

BIPHOSPHATE OF LEAD ( $PL + 2p'$ ) is deposited in granular crystals, by solutions of the preceding phosphates in phosphoric acid.

*Native Phosphate of Lead* has been found in the mines of Cumberland, Durham, Yorkshire, and of Wanlock Head, in Scotland. Its colour is various shades of green, yellow, and brown. Its primitive form is a rhomboid, but it usually occurs in six-sided prisms. It is semi-transparent and brittle. It appears to be a subsesquiphosphate of lead combined in variable proportions with chloride of lead.

NITROPHOSPHATE OF LEAD. A crystallized combination of phosphate and nitrate of lead is obtained by evaporating a solution of phosphate of lead in nitric acid. Water decomposes it and resolves it into its component salts. (Berzelius.)

SELENIURET OF LEAD. ( $pl + se.$ ) Lead and selenium readily combine and yield a white seleniuret, which has been found native in the Hartz and at Fahlun. It consists of

						H. Rose.
Lead . . .	1	..	104	..	72.22	.. 71.81
Selenium . .	1	..	40	..	27.78	.. 27.59
	<hr/>		<hr/>		<hr/>	<hr/>
	1		144		100.00	99.40

SELENITE OF LEAD. ( $PL + S\grave{e}.$ ) Selenious acid and the alkaline selenites occasion a white precipitate in solutions of lead, which falls in the form of a heavy powder. It is nearly as fusible as chloride of lead, and concretes on cooling into a white crystalline mass; it is almost insoluble in water, and difficultly decomposed by boiling sulphuric acid. It consists of

					Berzelius.
Oxide of lead . . . .	1	..	112	..	66.66
Selenious acid . . . .	1	..	56	..	33.33
	<hr/>		<hr/>		<hr/>
	1		168		100.00

CARBURET OF LEAD. The compounds described under this name are probably mixtures of finely-divided metallic lead and charcoal. They are obtained by decomposing tartrate of lead or cyanuret of lead in close vessels: the former has already been mentioned as a *pyrophorus*.

CARBONATE OF LEAD. ( $PL + CAR'$ .) When an alkaline carbonate is added to nitrate of lead, a white precipitate of *carbonate of lead* falls: it is tasteless, insoluble in water, but soluble in fixed alkaline solutions. Its sp. gr. is 6.4. It is employed as a white paint, under the name of *white lead* or *ceruse*, and is usually prepared by exposing sheet-lead to the action of the vapour of vinegar, or by decomposing acetate of lead by a carbonate. In this country it is largely manufactured by the latter method. (See *Acetate of Lead*.) In France and Sweden it is made by passing carbonic acid obtained by burning charcoal, through a solution of *subacetate* of lead; carbonate of lead falls, and the solution becomes a neutral acetate, which, by digesting with litharge, is again converted into the subsalt. Carbonate of lead consists of

				Berzelius.	Chevreul.	Klaproth.	Chenevix.
Oxide of lead . . .	1	. 112	. 83.58	. 83.5	. 83.64	. 83.67	. 85
Carbonic acid . . .	1	. 22	. 16.42	. 16.5	. 16.36	. 16.33	. 15
	<hr/>		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1	134	100.00	100.0	100.00	100.00	100

*Native Carbonate of Lead* is one of the most beautiful of the metallic ores: it occurs crystallized, and fibrous; the former transparent, the latter generally opaque. It is soft and brittle, and occasionally tinged green with carbonate of copper, or gray by sulphuret of lead. The octoëdron is its primitive form: it also occurs prismatic and tabular. It has been found in Cumberland and Durham; and the acicular variety, of great beauty, in Cornwall.

CYANURET OF LEAD ( $pl + cy$ ) falls in the form of an insoluble white powder when cyanuret of potassium is added to a solution of nitrate of lead, or when hydrocyanic acid is dropped into acetate of lead: heated to redness in a glass tube, it gives out nitrogen, and leaves the pyrophoric *carburet of lead* above noticed.

CYANATE OF LEAD ( $Pl + cy'$ ) is thrown down in the form of a white crystalline precipitate when cyanate of potassa is added to acetate of lead; it is anhydrous, and consists of 77 oxide + 23 acid. (Wöhler.)

SULPHOCYANURET OF LEAD forms rhomboidal crystals, which are slightly deliquescent.

FERROCYANURET OF LEAD. ( $fe + 2 pl + 3 cy.$ ) When nitrate of lead is decomposed by excess of ferrocyanuret of potassium a white precipitate falls, which, when dried and gently heated, loses water. In what may be termed its *hydrated state*, it consists, according to Berzelius, of 1 equivalent of hydrocyanate of protoxide of iron, and 2 equivalents of hydrocyanate of protoxide of lead; and, after having been heated, of

							Berzelius.
Iron . . . .	1	..	28	..	8.9	..	8.81
Lead . . . .	2	..	208	..	66.3	..	65.91
Cyanogen . .	3	..	78	..	24.8	..	23.89
	1		314		100.0		98.61

BORATE OF LEAD ( $Pl + bo'$ ) is precipitated in the form of a white powder, when borate of soda is mixed with nitrate of lead: it fuses into a colourless glass.

ALLOYS OF LEAD. With *potassium* lead forms a brittle and very fusible alloy: with *sodium* the compound is equally brittle, but less fusible. When exposed to air, these alloys suffer decomposition in consequence of the oxidizement of the alkaline bases. The alloy of lead and *manganese* has not been examined. When lead is fused with *iron*, two alloys are obtained; that at the bottom of the crucible consisting of lead with a little iron; while the superficial portion is iron with a little lead. (Guyton Morveau, *Ann. de Chim.*, lvii.) With *zinc*, lead forms a hard ductile alloy. Common  *pewter*  consists of about 80 parts of *tin* and 20 of lead. Equal parts of lead and tin constitute *plumbers' solder*; and what is termed *pot-metal* is an alloy of lead and *copper*.

CHARACTERS OF THE SALTS OF LEAD. The *soluble salts of lead* have a sweet austere taste, and are characterized by the white precipitate produced by ferrocyanuret of potassium, the black by sulphuretted hydrogen, the deep-brown by hydrosulphuret of ammonia, the yellow by iodide of potassium, and the white by sulphuric acid and the soluble sulphates. The *salts insoluble in water* are dissolved by soda and potassa, or by nitric acid, when the metal is rendered manifest by sulphuretted hydrogen

and other tests. Heated by the blowpipe upon charcoal, they afford a button of metal. Lead is precipitated from its solutions, in the metallic state, by many of the other metals. Zinc and Cadmium separate metallic lead from the nitrate: iron only effects its partial decomposition when in a very dilute state. Chloride of lead is slowly but entirely reduced by zinc, cadmium, and iron, but tin produces no effect except free muriatic acid be present. All the difficultly-soluble salts of lead may be decomposed and reduced, by mixing them with dilute muriatic acid, and immersing a plate of zinc in the liquid. Zinc, cadmium, and tin, decompose the *alkaline* solutions of oxide of lead, but iron is without action upon them. The appearance of the metallic lead, in these cases, depends upon the state of the solution, which, if concentrated, yields it in dull dendritic crystals, but if dilute, in large metallic leaves.

### § XVII. ANTIMONY.

THIS metal was first made known by Basil Valentine, towards the end of the 15th century. It is found *native* in Sweden, in France, and in the Hartz; but its principal ore is the *sulphuret*, the *stibium* of the ancients, which is found massive and crystallized, and of which there are several varieties. The most common is the *radiated*, which is of a gray colour, brittle, and frequently crystallized in four and six-sided prisms. This ore may be decomposed, and the pure metal obtained from it, by the following process: Mix three parts of the powdered sulphuret with two of crude tartar, and throw the mixture by spoonfuls into a red-hot crucible; then heat the mass to redness, and a button will be found at the bottom of the crucible, which is the metal as it commonly occurs in commerce, and is nearly pure. Reduce this button to fine powder, and dissolve it in nitromuriatic acid; pour this solution into water, which will occasion the precipitation of a white powder, which is to be washed and mixed with twice its weight of tartar, and exposed to a dull red-heat in a crucible. The button now obtained is pure antimony.

Antimony is of a silvery-white colour, brittle and crystalline in its ordinary texture. It fuses at about  $800^{\circ}$ , and is volatile at a very high heat. Its specific gravity is 6.712. (Hatchett, *Phil. Trans.*, 1803.) Placed upon ignited charcoal, under a current of oxygen gas, antimony burns with great brilliancy, throwing off its oxide in the form of a dense yellow smoke. The equivalent of antimony is 65. (64.5 Gmelin; 64.6 Turner.)

ANTIMONY AND OXYGEN. Much difference of opinion has prevailed among chemists respecting the number of the definite oxides of antimony: it is probable that there are at least three, of which one only, the protoxide, is salifiable. The composition of these oxides has also been variously stated, and much difficulty has occurred in assimilating them to the atomic theory: the most accurate and satisfactory experiments upon this subject are those of Berzelius, from which it would appear that the oxygen in the protoxide is to that in the peroxide, not as 1 to 2 but as 1.5 to 2.5, or as 3 to 5, and that in the three oxides, 1 atom of antimony is united with 1.5, 2, and 2.5 of oxygen.

PROTOXIDE OF ANTIMONY; SESQUIOXIDE OF ANTIMONY ( $an + 1\frac{1}{2}O$ ) is thus obtained: To 200 parts of sulphuric acid add 50 parts of powdered metallic antimony, boil the mixture to dryness, and wash the dry mass, first in water, and then with a weak solution of carbonate of potassa; a white powder remains, which, when thoroughly washed with hot water, is *protoxide of antimony*. It may also be procured by dissolving antimony in muriatic acid, pouring the solution into water, and washing the white precipitate with solution of carbonate of potassa or of soda. This oxide may also be obtained by adding ammonia to solution of tartrate of antimony and potassa, heating the mixture, and washing the precipitate in large quantities of boiling water. It is thus procured in the form of a heavy white powder.

Protoxide of antimony exists in all the active antimonial preparations; in emetic tartar, kermes, glass of antimony, golden sulphuret, &c. It is fusible and volatile at a red-heat, undergoing no change in close vessels; but if air be present, it undergoes a kind of combustion, and passes into the state of deutoxide. It is decomposed by sulphur and charcoal; and when acted on by nitric acid, is converted into peroxide; if heated with chlorate of potassa it deflagrates and also becomes peroxidized; it is very soluble in muriatic acid, and readily forms emetic tartar when boiled in solution of bitartrate of potassa. When recently precipitated, and digested in caustic potassa, it is partly converted into a gray powder, which is a true compound of the oxide and the alkali, very difficultly soluble. A similar combination may be obtained with soda and ammonia. When metallic antimony in fusion is exposed to a bright red-heat, it is converted into an oxide, which appears to be the protoxide, and which condenses in long and delicate needles when sublimed. This was formerly called *Argentine flowers of Antimony*. This is the only salifiable oxide of antimony: it consists of

					Proust.	Berzelius.	J. Davy.
Antimony	. . .	1 . . .	65 . . .	84.5 . . .	81.5 . . .	84.319 . . .	85
Oxygen	. . .	$1\frac{1}{2}$ . . .	12 . . .	15.5 . . .	18.5 . . .	15.681 . . .	15
		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
		1	77	100.0	100.0	100.000	100.

DEUTOXIDE OF ANTIMONY; ANTIMONIOUS ACID ( $an + 2O$ ) is the result of the above-mentioned combustion of the protoxide. It is also obtained by exposing the peroxide to a red-heat. It is white, but assumes a yellow colour when heated; fixed and infusible in the fire; insoluble in nitric acid, and nearly so in sulphuric acid. It readily combines with potassa by fusion, and the resulting compound (*antimonite of potassa*) dissolves in water, and furnishes, upon the addition of an acid, a white precipitate of *hydrated deutoxide*, which, when thoroughly edulcorated, has the property of reddening litmus. It consists of

					Proust.	Thenard.	Berzelius.	Thomson.
Antimony	. . .	1 . . .	65 . . .	80.25 . . .	77 . . .	80 . . .	80.127 . . .	80.84
Oxygen	. . .	2 . . .	16 . . .	19.75 . . .	23 . . .	20 . . .	19.873 . . .	19.16
		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
		1	81	100.00	100	100	100.000	100.00

PEROXIDE OF ANTIMONY; ANTIMONIC ACID ( $an + 2\frac{1}{2}O$ ) is procured by acting for a considerable time upon the powdered metal, by excess of hot nitric acid, and exposing the product to a heat of about 500°. The

*diaphoretic antimony* and *Bezoar mineral* of old *Pharmacopœiæ* consisted of this oxide, which, compared with the protoxide, is nearly inert. It is white, or pale-yellow, tasteless, and insoluble in water. It neither fuses nor volatilizes at a bright red-heat, but when exposed to the flame of a spirit-lamp urged by a blowpipe, it passes off slowly in white fumes, being partially reduced by the hydrogen of the flame. It does not decompose the alkaline carbonates in the humid way, but at a red-heat it expels their carbonic acid, and combines with the base. It dissolves in the liquid caustic alkalis, and in muriatic acid when in the state of hydrate; but after exposure to a dull red-heat becomes of extremely difficult solubility.

Peroxide of antimony may also be obtained by deflagrating a mixture of four parts of nitre, and one of powdered antimony, and washing the residue with nitric acid and water; or, by dissolving antimony in nitro-muriatic acid, and pouring the solution into water: it is thus, whenedulcorated, a hydrated peroxide, and may be dried nearly at a red-heat: at somewhat higher temperatures it loses oxygen and passes into deutoxide. It consists of

				Thenard.	Thomson.	Berzelius.	Proust.						
Antimony . . .	1	..	65	..	76.5	..	68	..	73.33	..	76.34	..	77
Oxygen . . .	2½	..	20	..	23.5	..	32	..	26.67	..	23.66	..	23
	1		85		100.0		100		100.00		100.00		100

ANTIMONIATE OF AMMONIA is formed by digesting peroxide of antimony in ammonia. On evaporation a *super-antimoniate of ammonia* is obtained in the form of a white powder.

ANTIMONIATE OF POTASSA is contained in the white powder obtained by igniting nitre and antimony. It dissolves in hot water, and this solution produces precipitates of insoluble antimoniates in several other metallic solutions.

ANTIMONY AND CHLORINE; PROTOCHLORIDE OF ANTIMONY; SESQUICHLORIDE OF ANTIMONY. ( $AN + 1\frac{1}{2}C$ .) The powdered metal takes fire when thrown into gaseous chlorine, and a compound, at first liquid, but afterwards concreting (if the antimony be in excess), is formed. This compound may be more definitely produced by the distillation of one part of powdered antimony with two and a half of perchloride of mercury; or by dissolving the protoxide of antimony in muriatic acid, and evaporating to dryness. The *protochloride* of antimony thus obtained, is a soft solid at common temperatures, but becomes liquid by a gentle heat, and crystallizes as it cools. It is the *butter of antimony* of old writers. It deliquesces by exposure to air; and is a powerful caustic. When water is added to this chloride of antimony, a mutual decomposition ensues, and hydrated protoxide of antimony, formerly called *Algarotti's powder*, or *mercurius vitæ*, and muriatic acid, result. This chloride consists of

				H. Rose.	Göbel.	J. Davy.					
Antimony . . .	1	..	65	..	54.7	..	53.27	..	54.98	..	60.42
Chlorine . . .	1½	..	54	..	45.3	..	46.73	..	45.02	..	39.58
	1		119		100.0		100.00		100.00		100.00

PERCHLORIDE OF ANTIMONY is formed by passing dry chlorine over heated antimony. It is a volatile transparent liquid, which emits copious fumes when exposed to air. When dropped into water a hydrated



peroxide of antimony falls, and muriatic acid is formed. (Rose, *Ann. of Phil.*, N. S., x.) It consists of

						H. Rose.
Antimony . . .	1	. .	65	. .	41.9	. . 40.56
Chlorine . . .	$2\frac{1}{2}$	. .	90	. .	58.1	. . 59.44
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	1		155		100.0	100.00

CHLORATE OF ANTIMONY has not been examined.

IODIDE OF ANTIMONY. Antimony and iodine combine when triturated together, and form a brown compound, fusible and volatile without decomposition; acted upon by water, it produces hydriodic acid and protoxide of antimony. It has not been analyzed.

IODATE OF ANTIMONY is unknown.

BROMIDE OF ANTIMONY. The action of bromine on antimony is attended by the disengagement of heat and light, and the compound is readily obtained by distillation, as in the process for preparing bromide of arsenic: it is solid at common temperatures; is fused at  $206^{\circ}$ , and boils at  $518^{\circ}$ . It is colourless, and crystallizes in needles; it attracts moisture from the air, and is decomposed by water. (Turner.)

SESQUIFLUORIDE OF ANTIMONY is a white solid compound, more volatile than sulphuric acid. (Dumas, *Ann. de Chim. et Phys.*, xxxi., 435.)

NITRIC ACID acts powerfully on metallic antimony, and, if mixed with it in fine powder, will sometimes cause its inflammation. The metal becomes peroxide, and scarcely an appreciable portion is retained in solution. As in some other cases of the vehement decomposition of nitric acid, ammonia is produced, which may be rendered sensible by pouring potassa on the white magma that results, and by which the nitrate of ammonia is decomposed. Protoxide of antimony, digested in dilute nitric acid, produces a difficultly-soluble salt, which separates in white scaly crystals, and which appears to be a *nitrate of antimony*.

NITRO-MURIATIC ACID readily dissolves antimony, and forms an orange-coloured solution, which is decomposed by the addition of water. Iron or zinc immersed into this solution throws down a black powder, which, according to Thenard, is pyrophoric.

SULPHURET OF ANTIMONY; SESQUISULPHURET OF ANTIMONY ( $2\text{An} + 1\frac{1}{2}\text{S}$ ) is easily formed by fusing the metal with sulphur. Its colour is dark-gray and metallic; its specific gravity 4.36. It closely resembles the *native sulphuret*. When this sulphuret is exposed under a muffle to a dull red-heat, it gradually loses sulphur, and absorbs oxygen, being converted into a gray powder, which consists of a mixture of protoxide of antimony and sulphuret. If the heat be increased, this fuses into a transparent substance of a yellow or brown colour, formerly called *glass of antimony*, the composition of which is variable; it generally contains about 85 *per cent.* of protoxide and 15 of sulphuret. In that which is imported for pharmaceutical purposes, from Germany and Holland, there is usually a portion of siliceous earth, and it is sometimes adulterated with oxide of lead. This fraud is detected by digesting the finely-powdered glass in hot nitric acid, diluting the solution, and filtering. The filtered liquor gives a white precipitate on the addition of sulphate of soda, if lead is present. During the formation of glass of antimony, if the heat be raised too high, the greater part of the oxide sublimes in slender crystalline

needles; while another portion, if air be not excluded, passes into the state of deutoxide, and undergoes no further change at a very high temperature. Compounds of the protoxide with larger quantities of the sulphuret have been termed *saffron of antimony* or *crocus metallorum*, and *liver of antimony*.

When sulphuret of antimony is deflagrated with nitre, the residue consists of sulphate and antimoniate of potassa. When boiled with sulphuric acid, sulphur is separated, sulphurous acid evolved, and a sulphate of antimony is formed from which water precipitates a subsulphate. With muriatic acid, sulphuretted hydrogen is evolved, and a solution of chloride of antimony in muriatic acid is formed together with more or less of the hydrosulphuretted oxide. Chlorine passed over heated sulphuret of antimony forms chloride of sulphur and sesquichloride of antimony. Hydrogen gas passed over this sulphuret at a red-heat carries off the sulphur in the form of sulphuretted hydrogen, and metallic antimony remains. Charcoal decomposes sulphuret of antimony at high temperatures, and sulphuret of carbon and metallic antimony are the results. This sulphuret of antimony, whether native or artificial, consists of

				Berzelius.	Bergman.	J. Davy.	Vauquelin.
Antimony . . .	1 . . .	65 . . .	73 . . .	72.8 . . .	74 . . .	74.16 . . .	75 . . .
Sulphur . . .	1½ . . .	24 . . .	27 . . .	27.2 . . .	26 . . .	25.84 . . .	25 . . .
	<u>1</u>	<u>89</u>	<u>100</u>	<u>100.0</u>	<u>100</u>	<u>100.00</u>	<u>100.</u>

**HYDROSULPHURETTED OXIDE OF ANTIMONY.** This compound has long been known under the name of *kermes mineral*; it is commonly prepared as follows: Equal parts of sulphuret of antimony and common potash are fused together; the resulting mass is finely powdered, and boiled in ten times its weight of water. The liquor is filtered while hot; and, during cooling, it deposits *kermes*. The mother-liquor of *kermes* deposits a copious yellowish-red precipitate upon the addition of dilute sulphuric acid, which, when washed and dried, is known under the name of *golden sulphur of antimony*.

In forming these compounds, it appears that the following changes take place. The sulphuret of antimony and potassium acts upon the water, a portion of which is decomposed; hydrosulphuret of potassa is formed, and hydrogen and oxygen unite to the sulphuret of antimony, producing a hydrosulphuretted oxide of that metal (*kermes*), which remains dissolved in the hot alkaline hydrosulphuret, and of which one portion is precipitated as that solution cools. When dilute sulphuric acid is added, the hydrosulphuret of potassa is decomposed, sulphate of potassa is formed, and sulphur and sulphuretted hydrogen are liberated; the sulphur falls in combination with the *kermes*, producing the *golden sulphur*, or sulphuretted-hydrosulphuret. Dr. Turner considers *kermes* and the golden sulphur as hydrated sulphurets of antimony, and not as hydrosulphuretted oxides; but their extreme activity as medicines seems to render the existence of protoxide in them probable. According to Rose (*Ann. of Phil., N. S., x.*), a *bisulphuret* and a *persulphuret* of antimony are precipitated when sulphuretted hydrogen is passed through a solution of antimonious and antimonie acids.

The whole question respecting the nature of *kermes* and the golden

sulphuret, is simplified by considering it merely in reference to the precipitation of solutions of the oxides of antimony by sulphuretted hydrogen. When a solution of emetic tartar (which contains the protoxide of antimony), acidulated by tartaric acid, is decomposed by sulphuretted hydrogen, an orange-coloured precipitate falls, which, when collected, thoroughlyedulcorated by hot water, and dried, is hydrosulphuretted protoxide of antimony.  $(an + 1\frac{1}{2} O) + 1\frac{1}{2} (S + h.)$  When heated, water is evolved and sesquisulphuret of antimony remains; or we obtain  $1\frac{1}{2} (h + O)$  and  $(an + 1\frac{1}{2} S)$ . When kermes is obtained by the other more complicated processes it varies in composition and in medicinal activity, containing a compound of oxide of antimony and potassa, and a portion of the double sulphuret of potassium and antimony, which is one of Berzelius' *sulphur salts*.

**SULPHURETTED OXIDE OF ANTIMONY.** It has already been stated that *glass of antimony* is a compound of sulphuret and oxide of antimony, and that some other medicinal preparations of antimony, contained in old pharmacopœiæ, are analogous combinations of variable proportions of the sulphuret and oxide. To this class of compounds belongs the beautiful and rare *ore* of antimony, called *red antimony*; it generally occurs in delicate capillary crystals, consisting, according to H. Rose, of 2 atoms of sesquisulphuret and 1 of sesquioxide of antimony.

**SULPHITE OF ANTIMONY** is an insoluble white salt, obtained by digesting the protoxide in sulphurous acid, or by passing sulphurous acid into protomuriate of antimony.

**SULPHATE OF ANTIMONY** is the white saline mass formed by boiling powdered antimony in sulphuric acid. Water resolves it into an insoluble *subsulphate* and a soluble *supersulphate*: the latter may be obtained in small deliquescent acicular crystals by evaporation.

**PHOSPHURET OF ANTIMONY** is formed by heating together equal parts of oxide of antimony, phosphoric acid, and charcoal. It is white and brittle. (Pelletier.)

Nothing is known respecting either the *Hypophosphite* or the *Phosphite* of antimony.

**PHOSPHATE OF ANTIMONY.** When protoxide of antimony is digested in phosphoric acid it is dissolved, but affords no crystallizable salt on evaporation.

**ANTIMONIAL POWDER.** In the *London Pharmacopœia* there is a preparation called *pulvis antimonialis*, formed by heating one part of sulphuret of antimony with two of hartshorn-shavings. The action of heat upon the sulphuret has already been described. Its effect upon the hartshorn-shavings is to destroy the animal matter, leaving little else than phosphate of lime. So that the *pulvis antimonialis* consists essentially of an oxide of antimony, mixed with phosphate of lime. This preparation is usually considered analogous to, if not identical with, *James's Powder*, which, according to Dr. Pearson's analysis (*Phil. Trans.*, 1791), consists of 43 phosphate of lime, and 57 oxide of antimony. Be this as it may, the antimonial powder of the *Pharmacopœia* is an uncertain and ill-contrived preparation: its activity depends upon the proportion of protoxide which it contains; but the greater part of the protoxide is apt to be volatilized, or converted into deutoxide, of a mixture of which, with

phosphate of lime, the antimonial powder generally consists. Accordingly, in examining Antimonial Powder from various sources, prepared after the direction of the *Pharmacopœia*, it is found of variable composition: and it is very difficult so to conduct the process as to obtain, upon the large scale, an uniform product. For medical use, *emetic tartar* seems the only certain and necessary preparation of antimony; if however, a compound of the nature of the Antimonial Powder be requisite, one of the best modes of preparing it would be to dissolve certain proportions of protoxide of antimony and phosphate of lime in muriatic acid, precipitate by ammonia, and edulcorate with a large quantity of water. Mr. Chenevix advises for this purpose equal parts of the oxide and phosphate, but such proportion of antimony is too great.

The following method furnishes, in the dry way, a tolerably uniform Antimonial Powder: burn two pounds of hartshorn to a cinder, reduce it to powder, and heat it to dull-redness in an iron pot: then gradually stir into it one pound of powdered sulphuret of antimony, added in successive portions, and continue the same heat as long as fumes arise; when these cease, the mixture will have a dirty-gray colour, and during the operation small crystals of oxide of antimony will be seen to collect upon its surface when a portion is taken out in an iron spoon. In this gray state it should be put into a covered crucible and heated to intense redness; a phosphorescent light of a greenish tint is soon perceived, and when this ceases the crucible may be removed from the fire, and its contents when cold reduced to a fine powder, which should be perfectly white.

Neither *carbonate*, *cyanuret*, nor *borate* of antimony are known to exist.

ALLOYS OF ANTIMONY. Antimony forms brittle alloys with the malleable metals. When *gold* was alloyed with  $\frac{1}{19\frac{1}{2}0}$  its weight of antimony, the compound was perfectly brittle; and even the fumes of antimony in the vicinity of melted gold are sufficient to destroy its ductility. (Hatchett, *Phil. Trans.*, 1803.) Silver is also rendered brittle by antimony. With *potassium* and *sodium* it forms white brittle compounds, destructible by the action of air and water. The *alloy of potassium and antimony* may be formed by heating to redness in a covered crucible a mixture of equal parts of finely-powdered antimony and tartar for about three hours. When cold, the crucible must be broken, the button of alloy freed from the scoriæ, broken into pieces, and preserved in a well-stopped phial. By substituting tartrate of soda for common tartar, the *alloy of sodium and antimony* may be obtained: and a mixture of soda-tartrate of potassa and powdered antimony, yields the *triple alloy of antimony, potassium, and sodium*. When these alloys are reduced to powder, and exposed to the air, they heat, and take fire like pyrophorus. The alloys of antimony with *manganese* and with *zinc* have not been examined.

Alloyed with *lead* in the proportion of 1 to 16, and a small addition of *copper*, antimony forms the alloy used for *printers' types*. With *lead* only, a white and rather brittle compound is formed, used for the plates upon which music is engraved. With *iron* it forms a hard whitish alloy, formerly called *martial regulus*, which may be obtained by fusing two parts

of sulphuret of antimony with one of iron-filings; a scoria consisting chiefly of sulphuret of iron is formed, and the fused alloy beneath usually presents a stellated appearance in consequence of its crystallization. This star, which upon large ingots is often beautifully distinct, was much admired by the alchemists, who considered it a mysterious guide to transmutation. With *tin*, antimony constitutes a kind of *pewter*, a term, however, which has also been applied to some other alloys, especially that of lead and tin. The finest pewter consists of about 12 parts of tin and 1 of antimony, with a small addition of copper. A good *white metal*, used for spoons and tea-pots, and sometimes called *Britannia metal*, is composed of 100 tin, 8 antimony, 2 bismuth, and 2 copper\*.

\* As a specimen of the *analysis* of antimonial compounds, I subjoin Mr. Hatchett's instructive examination of the *native triple sulphuret of lead, antimony, and copper*, or *Bournonite*.

A. 200 grains of the ore, reduced to a fine powder, were put into a glass matrass, and, two ounces of muriatic acid being added, the vessel was placed in a sand-bath. As this acid, even when heated, scarcely produced any effect, some nitric acid was gradually added, by drops, until a moderate effervescence began to appear. The whole was then digested in a gentle heat, during one hour; and a green-coloured solution was formed, whilst a quantity of sulphur floated on the surface, which was collected, and was again digested in another vessel, with half an ounce of muriatic acid. The sulphur then appeared to be pure, and, being well washed and dried on bibulous paper, weighed 34 grains: it was afterwards burned in a porcelain cup, without leaving any other residuum than a slight dark stain.

B. The green solution, by cooling, had deposited a white saline sediment; but this disappeared upon the application of heat, and the addition of the muriatic acid in which the sulphur had been digested. The solution was perfectly transparent, and of a yellowish-green: it was made to boil, and in this state was added to three quarts of boiling distilled water, which immediately became like milk; this was poured on a very bibulous filter, so that the liquor passed through before it had time to cool; and the white precipitate thus collected, being well edulcorated with boiling water, and dried on a sand-bath, weighed 63 grains.

C. The washings were added to the filtrated liquor; and the whole was gradually evaporated at different times,

between each of which it was suffered to cool, and remain undisturbed during several hours. A quantity of crystallized chloride of lead was thus obtained, until nearly the whole of the liquor was evaporated: to this last portion a few drops of sulphuric acid were added, and the evaporation was carried on to dryness; after which the residuum, being dissolved in boiling distilled water, left a small portion of sulphate of lead. The crystallized chloride of lead was then dissolved in boiling water; and, being precipitated by sulphate of soda, was added to the former portion, was washed, dried on a sand-bath, and then weighed 120.20 grains.

D. The filtrated liquor was now of a pale bluish-green, which changed to deep-blue, upon the addition of ammonia; some ochraceous flocculi were collected, and, when dry, were heated with wax in a porcelain crucible, by which they became completely attractable by the magnet, and weighed 2.40 grains.

E. The clear blue liquor was evaporated nearly to dryness; and, being boiled with strong lixivium of pure potash, until the whole was almost reduced to a dry mass, it was digested in boiling distilled water; and the black oxide of copper, being collected and washed on a filter, was completely dried, and weighed 32 grains.

200 grains of the ore, treated as here stated, afforded,

	Grains.
A. Sulphur . . . . .	34.
B. Oxide of antimony . . . . .	63.
C. Sulphate of lead . . . . .	120.20
D. Iron . . . . .	2.40
E. Black oxide of copper . . . . .	32.

But the metals composing this triple sulphuret are evidently in the metallic state; and antimony precipitated from

CHARACTERS OF THE SALTS OF ANTIMONY. When chloride of antimony is dropped into water, and the precipitate redissolved by muriatic acid, the solution is acted upon by reagents as follows:— Solutions of potassa, and of ammonia, and their carbonates, produce white precipitates, insoluble in excess of potassa. Oxalic acid, phosphate of soda, and ferrocyanuret of potassium produce white precipitates; the latter is insoluble in muriatic acid, and therefore not merely occasioned by the water of the reagent. Red ferrocyanuret of potassium (sesqui), produces no precipitate. Hydrosulphuret of ammonia produces a red precipitate, soluble in excess of the precipitant. Sulphuretted hydrogen produces a red precipitate in acid and in neutral solutions of protoxide of antimony; if the solution is neutral, the precipitate does not fall till heat is applied, or muriatic acid added. Metallic zinc precipitates metallic antimony in the form of a black powder. Cadmium, iron, cobalt, tin, lead, bismuth, and copper, also throw down the metal. The compounds of protoxide of antimony which are insoluble in water, are nearly all soluble in muriatic acid, and sulphuretted hydrogen is the most unequivocal test. (H. Rose.) Before the blowpipe, oxide of antimony is partly reduced in the exterior flame, and spreads a white smoke on the charcoal. In the interior flame it is readily reduced. With microcosmic salt and with borax it forms a hyacinth-coloured glass. Metallic antimony, when ignited on charcoal, becomes covered with acicular crystals of white oxide. Sulphuret of antimony melts on charcoal, and is absorbed.

### § XVIII. BISMUTH.

THIS metal was first described by Agricola in 1529. It was sometimes called *Marcasite*. It is found *native*, and combined with oxygen, and with arsenic and sulphur. It is neither of common occurrence nor very abundant. *Native Bismuth* occurs crystallized in octoëdra and cubes, and generally contains arsenic, and sometimes cobalt. It has been found in Cornwall, and in Germany, France, and Sweden.

The metal may be obtained pure, by dissolving the bismuth of commerce in nitric acid; water is added to the nitric solution, which separates *subnitrate of bismuth*. This compound is easily reduced in the usual way with a little black flux at a moderate heat.

Bismuth is a brittle white metal, with a slight tint of red: its specific gravity is 9.822. (Hatchett, *Phil. Trans.*, 1803.) It fuses at  $476^{\circ}$ , and always crystallizes on cooling. According to Chaudet, pure bismuth is somewhat flexible. A cast bar of the metal,  $\frac{1}{16}$ th of an inch diameter,

muriatic acid by water, is to metallic antimony as 130 to 100; therefore, the 63 grains of that oxide must be estimated at 48.46 grains of the metal. Again, sulphate of lead is to metallic lead as 141 to 100; therefore, 120.20 grains of the former are = 85.24 grains of the latter. And, lastly, black oxide of copper contains 20 *per cent.* of oxygen; consequently, 32 grains of the black oxide are = 25.60 grains of metallic

copper. The proportions for 200 grains of the ore will, therefore, be,

Sulphur . . . . .	34.
Antimony . . . . .	48.46
Lead . . . . .	85.24
Iron . . . . .	2.40
Copper . . . . .	25.60
	<hr/>
	195.70
	<hr/>
Loss . . . . .	4.30

supports, according to Muschenbroeck, a weight of forty-eight pounds. Bismuth is volatile at a high heat, and may be distilled in close vessels. It transmits heat more slowly than most other metals, perhaps in consequence of its texture.

**BISMUTH AND OXYGEN: PROTOXIDE OF BISMUTH.** (*bi + o.*) When bismuth is exposed to heat and air it oxidizes, forming a fusible *white oxide*. If the heat be increased by directing a current of oxygen upon the metal, it burns with much brilliancy, and produces an abundant yellow smoke, which condenses in the form of a yellowish-white sublimate. The readiest mode of obtaining oxide of bismuth, consists in dissolving bismuth in nitric acid, precipitating by dilution with water, edulcorating the precipitate, and heating it, when dry, to dull-redness. When in fusion, this oxide acts upon other oxides much in the same way as oxide of lead. It forms, on cooling, a vitreous mass of a specific gravity of 8.2. The equivalent of bismuth, deduced from the experiments of J. Davy on the chloride, and of Lagerhielm on the oxide, is 72, (71 Turner and Gmelin,) and the oxide consists of

					J. Davy.	Lagerhielm.	Klaproth.		
Bismuth	1	..	72	..	90	..	89.863	..	89.28
Oxygen	1	..	8	..	10	..	10.137	..	10.72
	<u>1</u>		<u>80</u>		<u>100</u>		<u>100.000</u>		<u>100.00</u>

Oxide of bismuth occurs, though very rarely, *native*: it has been found in Cornwall and Saxony.

**PEROXIDE OF BISMUTH: SESQUIOXIDE OF BISMUTH** (*bi + 1½o*). This oxide was first noticed by Bucholz and Brandes, but its nature and composition have been recently examined by A. Stromeyer. (Turner.) It is formed when hydrate of potassa is fused with protoxide of bismuth, or by gently heating the protoxide in a solution of chloride of potassa or soda: after washing with water, any unchanged protoxide is dissolved by a solution of 1 part of pure nitric acid in 9 of water. It is a heavy brown powder; it is not salifiable: heated with sulphuric or phosphoric acid, oxygen is evolved, and sulphate or phosphate of the protoxide is formed: with muriatic acid, chlorine is evolved, and a protochloride produced. (*Ann. de Chim. et Phys.*, li., 267.)

**CHLORIDE OF BISMUTH** (*bi + c*) is procured by gently heating the metal in chlorine; it burns with a blue flame, and forms a gray compound. This chloride may also be prepared by heating two parts of corrosive sublimate with one of powdered bismuth, and expelling the excess of the former and the mercury by heat; or by evaporating the solution of oxide of bismuth in muriatic acid to dryness, and heating the residue in close vessels. When nitrate of bismuth is decomposed by a solution of chloride of sodium, a white powder falls, which is either a *subchloride* or a compound of oxide of bismuth with the chloride. Chloride of bismuth was formerly called *Butter of Bismuth*. It is of a gray colour, and fuses at about 480°. In close vessels it does not sublime at a red-heat. When exposed to air it deliquesces. It consists of

					J. Davy.			
Bismuth	. .	1	..	72	..	66.6	..	66.4
Chlorine	. .	1	..	36	..	33.4	..	33.6
		<u>1</u>		<u>108</u>		<u>100 0</u>		<u>100.0</u>

CHLORATE OF BISMUTH has not been examined.

IODIDE OF BISMUTH ( $bi + i$ ), obtained by heating iodine with the metal, is of a brown colour, and insoluble in water. When hydriodic acid or iodide of potassium is added to nitrate of bismuth, a precipitate falls of a deep orange-colour, insoluble in water, but soluble in liquid potassa.

IODATE OF BISMUTH ( $Bi + i'$ ) is thrown down upon adding iodate of potassa to nitrate of bismuth. It is white, and insoluble. (Pleischl.)

BROMIDE OF BISMUTH ( $bi + b$ ) is a gray compound, obtained by the direct action of bromine upon powdered bismuth. It fuses at about  $400^\circ$ , and sublimes at a low red-heat. It is decomposed by water, and oxide of bismuth is formed. (Serullas.)

FLUORIDE OF BISMUTH ( $bi + f$ ) is soluble in water, and deposited, on evaporation, in the form of a white powder. (Berzelius.)

HYDRURET OF BISMUTH. When bismuth is made the negative electrode in water, black dendritical crystals are deposited upon it. (Ruhland, Schweigger's *Journal*, xv., 417.) This is probably metallic bismuth reduced by the hydrogen.

NITRATE OF BISMUTH. ( $Bi + n$ .) This salt is made by dissolving the metal to saturation in two parts of nitric acid and one of water: the action is rapid, and nitric oxide is copiously evolved. The solution affords four-sided prismatic crystals, which are decomposed at a red-heat, and leave oxide of bismuth. Ammonia occasions a precipitate in nitrate of bismuth, which is redissolved by excess of the alkali. Potassa and soda also throw down the oxide, which is but sparingly soluble in those alkalis. Nitrate of bismuth is decomposed by water, and a fine white powder, called *magistery of bismuth*, *pearl white*, or *blanc de fard*, is precipitated, which is a *hydrated subnitrate of bismuth*. In this state it has been used in medicine as a tonic. (*Quarterly Journal*, viii., 295.) If characters be written on paper with nitrate of bismuth they are invisible when dry, but become white and legible on immersion in water, thus forming a *white sympathetic ink*. The same characters are rendered brown or black by solution of sulphuretted hydrogen. It is sometimes stated, that the salts of bismuth are blackened by exposure to light, but such an effect depends upon their containing a minute portion of silver. The *crystallized nitrate* is a hydrated salt, composed of

						Berzelius.
Oxide of bismuth	1	..	80	..	49.7	.. 48.8
Nitric acid . . .	1	..	54	..	33.5	.. 33.7
Water . . . . .	3	..	27	..	16.8	.. 17.5
	1		161		100.0	100.0

The *subnitrate*, formed by the action of water on the nitrate, and dried at  $212^\circ$ , consists of

						Grouvelle.
Oxide of bismuth	4	..	320	..	81.7	.. 81.37
Nitric acid . . .	1	..	54	..	13.8	.. 13.97
Water . . . . .	2	..	18	..	4.5	.. 4.66
	1		392		100.0	100.00

SULPHURET OF BISMUTH ( $bi + s$ ) is of a blueish colour and metallic lustre; it is less fusible than bismuth, and is reduced by hydrogen at a



red-heat, sulphuretted hydrogen being evolved. (H. Rose.) It consists of

						Lagerhielm.	J. Davy.	H. Rose. Native.	
Bismuth	1	..	72	..	81.8	..	81.619	..	80.98
Sulphur	1	..	16	..	18.2	..	18.381	..	18.72
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		88		100.0		100.000		100.00

*Native Sulphuret of Bismuth* has been found in Cornwall, Bohemia, Saxony, and Sweden. It occurs massive and acicular, its lustre is metallic, and its colour blueish-gray. It is a very rare mineral.

HYDROSULPHURET OF BISMUTH ( $Bi + hS'$ ) is thrown down in the form of a dark-brown powder, when the salts of bismuth are decomposed by sulphuretted hydrogen, or by an alkaline hydrosulphuret.

HYPOSULPHITE OF BISMUTH has not been examined.

SULPHITE OF BISMUTH ( $Bi + S$ ) is an insoluble white powder, which is not taken up by excess of the acid. (Fourcroy.)

HYPOSULPHATE OF BISMUTH has not been examined.

SULPHATE OF BISMUTH ( $Bi + S'$ ) is obtained by dissolving the oxide in sulphuric acid and evaporating to dryness, or by heating powdered bismuth in sulphuric acid. It is a white compound, insoluble in, but decomposed by, water, which converts it into a *subsulphate* and *super-sulphate*. The *sulphate* consists of

						Lagerhielm.	
Oxide of bismuth	1	..	80	..	66.6	..	66.35
Sulphuric acid	1	..	40	..	33.4	..	33.65
	<hr/>		<hr/>		<hr/>		<hr/>
	1		120		100.0		100.00

The *subsulphate* consists of

						Berzelius.	
Oxide of bismuth	3	..	240	..	85.9	..	85.5
Sulphuric acid	1	..	40	..	14.1	..	14.5
	<hr/>		<hr/>		<hr/>		<hr/>
	1		280		100.0		100.0

PHOSPHURET OF BISMUTH ( $bi + p$ ) does not, according to Pelletier, exist; at least, it cannot be formed by the usual process of projecting phosphorus upon the hot metal. When phosphuretted hydrogen gas is passed into nitrate of bismuth, a dark-brown precipitate ensues, which, when collected and distilled, loses the whole of its phosphorus.

Neither the *hypophosphite*, nor *phosphite*, have been examined.

PHOSPHATE OF BISMUTH is formed, according to Wenzel, by digesting the oxide in phosphoric acid; an insoluble subphosphate, and a soluble and crystallizable phosphate, are the results.

SELENURET OF BISMUTH is a silver-white compound.

CARBONATE OF BISMUTH is thrown down from the nitrate by carbonated alkalis: it is a white powder, insoluble in carbonic acid, and probably a *subcarbonate*.

CYANURET OF BISMUTH has not been formed. *Ferrocyanuret* of Bismuth, formed by double decomposition, is a white or yellowish powder, soluble in nitric acid, and precipitated again by water. (Ittner.) The red ferrocyanuret (*ferrosesquicyanuret*) of potassium produces a brown precipitate in nitrate of bismuth.

BORATE OF BISMUTH is a white powder, insoluble in water.

ALLOYS OF BISMUTH. Bismuth forms alloys, some of which are remarkable for their fusibility. With *gold*, *platinum*, and *silver*, it forms brittle compounds. A compound of 8 parts of *bismuth*, 5 of *lead*, and 3 of *tin*, liquefies at  $212^{\circ}$ ; it is called Sir I. Newton's *fusible metal*. The addition of one part of *mercury* renders it yet more fusible. Bismuth enters into the composition of *soft solders*. These alloys are mostly white, brittle, and easily oxidated. Combinations of bismuth with *potassium* and *sodium* may be obtained by the same process as the corresponding alloys of antimony.

CHARACTERS OF THE SALTS OF BISMUTH. In the clear acid solutions of oxide of bismuth, potassa and ammonia, and their carbonates, produce white precipitates, insoluble in excess of the precipitant. Hydrosulphuret of ammonia and sulphuretted hydrogen produce brown or black precipitates, easily reduced to metallic bismuth when mixed with soda, and fused in the inner flame of the blowpipe. Chloride and nitrate of bismuth are decomposed by the immersion of plates of zinc, cadmium, tin, iron, and lead: the metal is commonly thrown down in the form of a black crystalline powder, except by iron, which at first produces it with metallic lustre. Before the blowpipe, oxide of bismuth melts readily, in a spoon, to a brown glass, which becomes brighter as it cools. With microcosmic salt it forms a gray-yellow glass, which loses its transparency, and becomes pale when cool: add a further proportion of oxide, and it becomes opaque. With borax it forms a gray glass, which decrepitates in the interior flame, and the metal is reduced and volatilized. It is readily reduced by itself on charcoal.

## § XIX. URANIUM.

URANIUM was discovered by Klaproth in 1789, and named after the planet discovered by Herschel in the same year. Its ores are few and scarce. The *native phosphate* is contained in the mineral termed *Uranite*, or *Uranitic Mica*. Its crystalline form is the cube, and several modifications; it often occurs in thin quadrangular plates. It exhibits various shades of yellow and green. It has been found in France; and of great beauty near Callington, in Cornwall. The *ferriferous oxide of uranium* was formerly mistaken for an ore of zinc, and called *Pechblende*, till Klaproth, in 1789, demonstrated it to contain uranium. It is a compound of protoxide of uranium and iron, with lead, copper, and other substances. From this ore uranium may be obtained by the following process: Reduce it to powder, and expose it to heat in a muffle; then digest in nitric acid, diluted with four parts of water, taking care to employ excess of the mineral, by which the solution of the iron is nearly prevented. The nitric solution is filtered, and sulphuretted hydrogen passed through it to throw down lead and copper; the clear solution being poured off, is boiled, filtered, and evaporated, and crystals of nitrate of uranium are deposited: when these are heated they are decomposed, and at a red-heat, protoxide of uranium remains.

Uranium was obtained, by Arfwedson, by passing hydrogen over the protoxide, heated in a glass tube. It is crystalline, of a metallic lustre,

of a gray-brown colour, brittle, and very difficult of fusion; its specific gravity has not been ascertained with precision. Bucholz states it as = 9.0. (Gehlen's *Journal*, iv.) Hitherto few experiments have been made upon this metal. It appears susceptible of two degrees of oxidizement, and its equivalent, deduced from the experiments of Arfwedson, Berzelius, and Schönberg, may be estimated at about 217.

PROTOXIDE OF URANIUM ( $UR + O$ ) is obtained by strongly heating the pernitrate: it is of a dark-green colour; it is very feebly acted on by the greater number of the acids, and the solutions and salts are green: nitric acid converts it into peroxide. When it is precipitated in the form of *hydrate*, by caustic potassa, it is much more soluble, but, if boiled, it loses water, and becomes dark-coloured and difficultly soluble. When precipitated by carbonate of ammonia it redissolves in excess of that precipitant, and forms a green solution. Protoxide of uranium consists of

					Schönberg.	Bucholz.	Arfwedson.	Berzelius.					
Uranium	1	..	217	..	96.44	..	94	..	95.1	..	96.443	..	96.446
Oxygen	1	..	8	..	3.56	..	6	..	4.9	..	3.557	..	3.554
	<u>1</u>		<u>225</u>		<u>100.00</u>		<u>100</u>		<u>100.0</u>		<u>100.000</u>		<u>100.000</u>

PEROXIDE OF URANIUM: SESQUIOXIDE OF URANIUM: URANIC ACID. ( $UR + 1\frac{1}{2} O$ .) When a solution of nitrate of uranium is precipitated by caustic potassa, a yellow powder falls, which was regarded as a pure hydrated peroxide, but it always retains potassa, so that the peroxide of uranium appears to act the part both of base and acid; if other precipitants are employed, they also are in part carried down by it, and the peroxide cannot thus be obtained pure. As thrown down by potassa, it is soluble in the carbonated alkalis, with which it forms double salts; and we are thus enabled to separate uranium from iron. Peroxide of uranium is not precipitated by sulphuretted hydrogen; a strong heat decomposes it, and converts it into protoxide: it is sometimes used to produce a deep-yellow upon porcelain. Arfwedson has shown that when the combinations of peroxide of uranium with baryta or with the oxides of iron, lead, or copper, are heated in a stream of hydrogen, water is formed; and the residue, cooled in hydrogen, takes fire on exposure to air.

The statements of different chemists respecting the composition of these oxides are much at variance. According to Thomson, the equivalent of uranium is 208, that of the protoxide 216, and of the peroxide 224; but Berzelius and Arfwedson (*Ann. of Phil.*, N. S., ii.) state that the oxygen in the protoxide is to that in the peroxide as 1 to 1.5; hence the composition of the latter appears to be

					Arfwedson.	Schönberg.			
Uranium	1	..	217	..	94.76	..	94.733	..	91.3
Oxygen	$1\frac{1}{2}$	..	12	..	5.24	..	5.267	..	8.7
	<u>1</u>		<u>229</u>		<u>100.00</u>		<u>100.000</u>		<u>100.0</u>

The mineral called *uranitic ochre* is generally considered as a *hydrated peroxide*.

CHLORIDES OF URANIUM. When the muriatic solutions of the oxides of uranium are evaporated to dryness, and heated in a small retort, they lose water, and *chlorides* remain, which are readily soluble in water,

alcohol, and ether. The ethereal solution of the perchloride, exposed to light, becomes dirty-green and turbid. These chlorides correspond in composition with the oxides.

POTASSA-CHLORIDE OF URANIUM crystallizes from its concentrated solution, and forms a triple salt, soluble in alcohol.

The action of *iodine*, *bromine*, and *fluorine* upon uranium has not been examined.

NITRATE OF URANIUM, formed as above directed, yields yellow prismatic and tabular crystals, very soluble, and somewhat deliquescent in a moist air. They are also readily soluble in alcohol and ether, and when the latter solution is exposed to light, it is decomposed, becomes green, and deposits the protoxide. They consist of

					Bucholz.	Brande.
Peroxide of uranium	1	..	229	..	62.91	.. 61
Nitric acid . . . .	1½	..	81	..	22.25	.. 25
Water . . . . .	6	..	54	..	14.84	.. 14
	<hr/>		<hr/>		<hr/>	<hr/>
	1		364		100.00	100
						60.7
						39.3
						<hr/>
						100.0

SUBNITRATE OF URANIUM, upon the authority of Bucholz, is formed by heating the nitrate, which renders a part insoluble in water, and separates in the form of a yellow powder.

AMMONIO-NITRATE OF URANIUM is a yellow crystallizable salt.

SULPHURET OF URANIUM was obtained by Rose, by passing the vapour of sulphuret of carbon over the protoxide, at a high heat. The alkaline hydrosulphurets form black precipitates in the pure solutions of uranium.

PROTOSULPHATE OF URANIUM forms green prismatic crystals: it may be formed by boiling the protoxide in sulphuric acid. With sulphate of potassa it produces a triple salt.

PERSULPHATE OF URANIUM forms yellow prismatic crystals, decomposable by heat, and, according to the analysis of Bucholz, consisting of 70 oxide, 18 acid, 12 water, = 100. Its alcoholic solution becomes ethereal and green when exposed to the sun's rays, and deposits a precipitate, which is a subsulphate of the protoxide. According to John, these sulphates are occasionally found *native*. (*Ann. of Phil.*, viii., 390, 2nd series.)

POTASSA-PERSULPHATE OF URANIUM. When a mixture of persulphate of uranium and sulphate of potassa is evaporated to crystallization, yellow granular crystals are obtained, composed, according to Berzelius, of

Potassa . . . . .	3	..	144	..	16.34
Peroxide of uranium	2	..	458	..	52.85
Sulphuric acid . . .	6	..	240	..	27.69
Water . . . . .	3	..	27	..	3.12
	<hr/>		<hr/>		<hr/>
	1		869		100.00

PHOSPHURET OF URANIUM has not been examined.

PERPHOSPHATE OF URANIUM is thrown down by phosphoric acid from the *peracetate*: it is a difficultly-soluble yellow salt: it is soluble in excess of phosphoric acid, and in carbonate of ammonia. (Laugier, *Ann. de Chim. et Phys.*, xxiv., 239.) It exists *native* in the micaceous ore of uranium. It consists of

Peroxide of uranium	1	..	229	..	62.91	..	Laugier, 61.
Phosphoric acid	1½	..	54	..	14.84	..	16.6
Water	9	..	81	..	22.25	..	22.
	<hr/>		<hr/>		<hr/>		<hr/>
	1		364		100.00		99.6

PERCARBONATE OF URANIUM is precipitated by a carbonated alkali from the solutions of the peroxide, but it loses carbonic acid on drying.

CYANURET OF URANIUM is thrown down in the form of a yellow powder, by solutions of cyanuret of potassium.

FERROCYANURET OF URANIUM is thrown down in the form of a rich brown, and very characteristic precipitate: in colour, it much resembles the ferrocyanuret of copper.

CHARACTERS OF THE SALTS OF URANIUM. The *protosalts* of uranium have a green, and the *persalts* a yellow colour, and an astringent metallic taste. Potassa forms in the solutions of the latter a yellow precipitate, and carbonate of potassa a straw-coloured precipitate: both these precipitates are insoluble in excess of pure alkali, but dissolve in the alkaline carbonates. Ferrocyanuret of potassium and tincture of galls produce brown precipitates in solutions of uranium. The salts are mostly soluble in alcohol and in ether, and acquire a green colour by exposure to the sun's rays. The protosalts have been very little examined. Uranium is not thrown down in a metallic state by any of the other metals. Before the blowpipe the peroxide of uranium becomes green or greenish-brown. With microcosmic salt in the interior flame it forms a clear yellow glass, the colour of which becomes more intense when cold. If long exposed to the exterior flame, and frequently cooled, it gives a pale yellowish-red or brown glass, which becomes greenish as it cools. With borax in the interior flame, a clear, colourless, or faintly green glass is formed, containing black particles, which appear to be the metal in its lowest state of oxidation. In the exterior flame this black matter is dissolved, if the quantity be not too great, and the glass becomes bright yellowish-green, and after further oxidation yellowish-brown. If brought again into the interior flame, the colour gradually changes to green, and the black matter is again precipitated, but no further reduction takes place.

## § XX. TITANIUM.

TITANIUM was first recognised as a distinct substance by Mr. Gregor; some of its compounds were also examined by Klaproth, who named it *Titanium*, after the Titans of ancient mythology. (See his Analysis of the Red Schorl of Hungary, *Beiträge*, i., 233.). For our knowledge of the properties of *Titanium* in its metallic state we are chiefly indebted to Dr. Wollaston, who discovered it in small cubic crystals, having the lustre of burnished copper, in the slag of the iron-furnaces at Merthyr Tydvil, in South Wales, (*Phil. Trans.*, 1823, p. 17.) These crystals, which have been found in similar slags from other sources, are titanium, almost absolutely pure: they have the following properties: They are so hard as to scratch rock-crystal; they are not acted on by nitric, muriatic,

or sulphuric acids, nor are they soluble in nitro-muriatic acid. Before the blowpipe they are infusible; they are, however, superficially oxidized by a continued heat, becoming of a purple or red colour. Borax has no action on them, but only removes the superficial oxide. Nitre oxidizes them on the surface. The combined action of nitre and borax soon effects their solution; but as these salts do not unite by fusion, the addition of soda accelerates their action. The fused mass becomes opaque on cooling by the deposit of a white oxide, which may either be previously freed of the salts by boiling water, and then dissolved in muriatic acid, or the whole mass may be at once dissolved together. In either case, alkalis precipitate from the solution a white oxide, insoluble in excess of alkali, either pure or carbonated. By evaporating the muriatic solution to dryness at  $212^{\circ}$ , it is freed of redundant acid, and a soluble muriate remains, in a favourable state for exhibiting the characteristic properties of the metal.

Titanium exists in the state of oxide in the minerals called *titanite* and *menachanite*. *Titanite* is a nearly pure oxide of titanium; it is of a brown colour, and occurs embedded in the quartz and granite of primitive countries, and sometimes traverses rock-crystals in fine hair-like filaments. In this country, it occurs at Beddgelert, in Caernarvonshire; and near Killin, in Scotland. The finest specimens are those from the vicinity of Mont Blanc and St. Gothard. The mineral, known by the name of *anatase*, *octoëdrite*, and *oysanite*, is nearly of the same nature as titanite. It is found in Bavaria, Norway, Switzerland, and in the valley of Oysans in France. *Menachanite* consists principally of oxides of titanium and iron; it is found in the bed of a small stream at Menachan, in Cornwall. *Nigrine*, *iserine*, *rutilite*, and *sphene*, are also ores of titanium.

According to Laugier (*Ann. de Chim.*, lxxxix., 306), the metal may be obtained from *titanite* by fusion with potassa; the fused mass, washed with water, leaves oxide of titanium, containing a little iron; it is to be dissolved in muriatic acid, and precipitated by oxalic acid. The oxalate affords the metal by intense ignition with charcoal: it is, however, not possible to obtain it in any state of agglutination. From *menachanite*, white oxide of titanium may be obtained by fusing it with potassa, and adding muriatic acid to the alkaline solution, so as merely to neutralize the alkali and precipitate the oxide; to separate a little adhering iron, this must be dissolved in excess of muriatic acid, and precipitated by oxalic acid as before.

Liebig prepares metallic titanium by putting fragments of recently-made chloride of titanium and ammonia into a glass tube, half an inch wide and two or three feet long, transmitting through it a current of perfectly dry ammonia, and, when atmospheric air is entirely displaced, applying heat until the glass softens: complete decomposition ensues, nitrogen gas is disengaged; hydrochlorate of ammonia sublimes, and metallic titanium is left in the state of a dark blue-coloured powder. If exposed to the air while warm, it is apt to take fire. (Turner.)

The equivalent of titanium has not been very satisfactorily determined; Gmelin adopts 31, Dr. Turner 24.3, Dr. Thomson 26; I have assumed 24, as the whole number, which, according to Dr. Turner, is most consistent with the experimental results of Rose.

OXIDES OF TITANIUM. Titanium appears to be susceptible of two degrees of oxidizement. The mineral called *anatase*, is regarded as the *protoxide*, but its composition has not been determined with accuracy. When peroxide of titanium is intensely heated with charcoal, or when a plate of zinc is immersed in a solution of chloride of titanium, a purple powder is obtained, which appears to consist of

Titanium . . . .	1	..	24	..	75
Oxygen . . . .	1	..	8	..	25
	1		32		100

PEROXIDE OF TITANIUM: TITANIC ACID ( $Ti + 2O$ ) may be obtained from *rutilite*, by fusing it in fine powder, in a platinum crucible, with thrice its weight of pure carbonate of potassa: a gray mass is obtained, which, after having been washed with water, is dissolved in muriatic acid, and on diluting with water, and boiling the solution, the greater part of the oxide of titanium is precipitated; it is collected, and washed with very dilute muriatic acid. In this state it still is apt to retain traces of iron and manganese, which may be separated by digesting the moist precipitate with hydrosulphuret of ammonia, which forms sulphurets with the iron and manganese, but does not affect the oxide of titanium. Dilute muriatic acid removes the sulphurets; and the oxide of titanium, after being again washed and heated red-hot, is pure. (Rose, *Ann. de Chim. et Phys.*, xxiii.)

*Titaniferous Oxide of Iron*, which is more abundant than *rutilite*, may also be used as a source of titanium; it is pulverised, washed, and exposed at a high red-heat in a porcelain tube to the action of a current of dry sulphuretted hydrogen, as long as water is evolved: the oxide of iron is converted into sulphuret, but the oxide of titanium undergoes no change: the product, when cold, is digested in muriatic acid, which leaves titanitic acid mixed with sulphur, from which it may be freed by heat; but as it still retains some iron, it must be again subjected to the action of the current of sulphuretted hydrogen in the porcelain tube; if afterwards treated by muriatic acid, well washed, and ignited, it is white and pure. (Rose, *Ann. de Phys.*, lxxxviii., and *Ann. de Chim. et Phys.*, xxxviii., 131.)

This oxide of titanium is white, and very infusible, and difficult of reduction: when recently precipitated it dissolves in some of the acids, but becomes nearly insoluble after it has been ignited. Its solution in muriatic acid is always very sour, and part of the oxide falls down when it is heated to the boiling-point, but by careful evaporation to dryness, a soluble chloride remains. It is precipitated by the pure and carbonated alkalis; infusion of galls, and ferrocyanuret of potassium throw it down of a characteristic red colour. When a rod of zinc is immersed in the muriatic solution of peroxide of titanium, a purple precipitate (probably of the protoxide) is obtained; but it acquires oxygen, and becomes white. The recently-precipitated peroxide is with difficulty separated from water upon a filter, but passes through in a milky state; the addition of a little acid or alkali facilitates its separation. It seems doubtful whether this oxide forms any definite salts with the acids: it unites with the alkalis, and has thence been termed *titanic acid*. It probably consists of

Titanium . . . .	1	..	24	..	60
Oxygen . . . .	2	.	16	..	40
	<hr/>		<hr/>		<hr/>
	1		40		100

CHLORIDE OF TITANIUM was obtained by Mr. George, (*Annals of Phil.*, N. S., ix., 18,) by passing dry chlorine over metallic titanium, heated to redness. It is a dense, transparent, and colourless fluid, fuming when exposed to air. It boils at a little above  $212^{\circ}$ , and acts violently upon water, evolving chlorine, and furnishing, when the water is not in excess, a white salt, very soluble, and deliquescent.

The density of its vapour is, according to Dumas, (*Ann. de Chim. et Phys.*, xxxiii., 388,) 6.836, and considering one volume of this vapour as composed of one volume of titanium vapour, and two volumes of chlorine, he deduces the equivalent of titanium = 26.4. When this chloride is exposed to ammoniacal gas it absorbs it, and becomes solid, forming the compound from which Liebig, as above stated, obtained metallic titanium. Assuming this to be a *bichloride*, it consists of

Titanium . . . .	1	..	24	..	25
Chlorine . . . .	2	..	72	..	75
	<hr/>		<hr/>		<hr/>
	1		96		100

FLUORIDE OF TITANIUM. The peroxide of titanium readily dissolves in hydrofluoric acid. When this solution is saturated with potassa and evaporated, a *titanofluoride of potassium* is the result, composed, according to Berzelius, of 1 atom of biffuoride of titanium + 1 atom of fluoride of potassium. Many other protoxides may be substituted for potassa; and hence the class of double salts which have been termed *titanofluorides*.

SULPHURET OF TITANIUM was obtained by M. Rose, by passing the vapour of sulphuret of carbon over peroxide of titanium. It has a dark-green colour and metallic lustre. (*Quarterly Journal*, xvi., 97.) It is stated to consist of

Titanium . . . .	1	..	24	..	42.8
Sulphur . . . .	2	..	32	..	57.2
	<hr/>		<hr/>		<hr/>
	1		56		100.0

PHOSPHURET OF TITANIUM is formed, according to Chenevix, by heating the phosphate with charcoal; it has a white metallic lustre, and is brittle.

PHOSPHATE OF TITANIUM falls when phosphoric acid is added to solution of peroxide of titanium in muriatic acid, in the form of a bulky white precipitate, which dries into a gummy mass. (H. Rose.)

TITANIATE OF POTASSA. The peroxide of titanium may be united by fusion with several bases, forming a class of compounds which have been termed *Titaniates*. When thus fused with potassa it yields a compound, from which water abstracts potassa, and leaves a white powder, composed of 18 potassa + 82 peroxide of titanium, and which is soluble in muriatic acid. (H. Rose.)

CHARACTERS OF THE SALTS OF TITANIUM. Titanium is not thrown down in the metallic state by any other metal. The bulky red precipitate



which its solutions afford with infusion of galls, is very characteristic: the other properties of its compounds will be evident from the preceding paragraphs. Before the blowpipe, oxide of titanium becomes yellowish when ignited in a spoon, and upon charcoal dark-brown. With micro-cosmic salt it gives in the interior flame a fine violet-coloured glass, more tending to blue than that from manganese. In the exterior flame this colour disappears. With borax it gives a dirty hyacinth-colour.

### § XXI. CERIUM.

THIS metal, which is named after the planet Ceres, was obtained, in 1803, by Hisinger and Berzelius, from a mineral found at Bastnas in Sweden, to which they have given the name of *cerite*. It was originally, in consequence of its density, called *heavystone* (*schwerstein*), and was considered by Klaproth as containing a peculiar earth, which he called *ochroit*. Cerium also occurs in *gadolinite*, and several other minerals of Fahlun; and in *orthite*, which is not an uncommon ingredient of Scandinavian granite. It is also contained in *Allanite*, a mineral from Greenland, first distinguished as a peculiar species by Mr. Thomas Allan, of Edinburgh. It contains, according to Dr. Thomson's analysis, about 40 *per cent.* of oxide of cerium.

To obtain cerium, the ore is calcined, pulverized, and digested in nitro-muriatic acid. To the filtered solution, from which part of the excess of acid has been boiled off, oxalic acid is added, which occasions a white precipitate: this, when dried and ignited, is *peroxide of cerium*, but it is extremely difficult of reduction. Mr. Children succeeded in fusing it by the aid of his powerful Voltaic apparatus, and when intensely heated it burned with a vivid flame, and was partly volatilized. Vauquelin describes cerium as a hard white brittle metal, (*Ann. de Chim.*, iv.) and as only soluble in nitromuriatic acid. Mosander obtained it by heating the dry chloride with potassium; violent action ensues, and a gray alloy of cerium and potassium results, which evolves hydrogen when put into water, and leaves the cerium in the form of a gray metallic powder, which, when dried and heated, burns brilliantly into an oxide, and is soluble in the weakest acids with the evolution of hydrogen. The equivalent of cerium may be assumed as 48. (46 Gmelin and Turner.)

PROTOXIDE OF CERIUM ( $CE + O$ ) is white, and may be obtained by precipitation from its muriate: it forms salts with the acids, from which the alkalis throw down a white hydrate; the carbonated alkalis a white carbonate, soluble in excess of the precipitant; and oxalate of ammonia a white oxalate.

Berzelius obtains protoxide of cerium as follows:—Cerite (composed according to Hisinger, of 68.6 oxide of cerium, 18 silica, 1.25 lime, 2 oxide of iron, and 9.75 water,) is boiled in nitromuriatic acid, and the solution evaporated to dryness. The residue, after having been gently heated, is again dissolved in water, and the solution precipitated by benzoate of ammonia, which throws down the iron: the remaining solution is precipitated by caustic ammonia, and the precipitate (which is a mixture of the oxides of cerium) dissolved in muriatic acid, evaporated to dryness and heated to redness in a retort as long as it smells of

chlorine. The residuary salt is dissolved in water and precipitated by caustic potassa. This precipitate, which is *hydrated protoxide of cerium*, presently becomes yellow by exposure to air, and cannot be obtained free from water, for all attempts to dry it are attended by its partial peroxidizement. Protoxide of cerium consists of

Cerium . . . . 1	..	48	..	85.7	..	Hisinger.
Oxygen . . . . 1	..	8	..	14.3	..	85.19
	<hr/>			<hr/>		14.81
	1	56		100.0		100.00

SUBPEROXIDE OF CERIUM? (*Ceroxyd-oxidul* of Berzelius) is obtained by subjecting the peroxide of cerium at a red-heat to the action of hydrogen gas; or by subjecting the oxalate or carbonate of the protoxide of cerium to a white-heat. It is a lemon-yellow powder, soluble in muriatic acid with the evolution of chlorine, and which, when heated in the air, becomes peroxide. It has not been analyzed.

PEROXIDE OF CERIUM; SESQUIOXIDE OF CERIUM. ( $ce + 1\frac{1}{2}o$ .) When protonitrate of cerium is decomposed at a red-heat, or when protocarbonate of cerium is heated in the air, this oxide is obtained in the form of a red powder. It is soluble in the acids, and when acted on by muriatic acid, it evolves chlorine: these solutions, when decomposed by potassa, afford a bulky precipitate of *hydrated peroxide of cerium*; it is pale-yellow when moist; dark-yellow when dried. Ammonia generally throws down *subsals* from these solutions. The moist hydrate is insoluble in the caustic alkalis. This oxide consists of

Cerium . . . . 1	..	48	..	80	..	Hisinger.
Oxygen . . . . $1\frac{1}{2}$	..	12	..	20	..	79.31
	<hr/>			<hr/>		20.69
	1	60		100		100.00

CHLORIDE OF CERIUM. ( $ce + c$ .) When the solution of the protoxide in muriatic acid is evaporated to dryness, a deliquescent *protochloride* is obtained, which is readily soluble in water and in alcohol; the latter solution burns with a green sparkling flame. The peroxide of cerium also dissolves in muriatic acid, furnishing a brown solution: but when it is gently heated chlorine is evolved, and a protochloride formed. Chloride of cerium consists of

Cerium . . . . 1	..	48	..	57.2
Oxygen . . . . 1	..	36	..	42.8
	<hr/>			<hr/>
	1	84		100.0

FLUORIDE OF CERIUM ( $ce + f$ ) is an insoluble yellow powder; it has been found *native* in the mines of Fahlun, in Sweden; and it exists in the mineral called *ytthrocerite*, combined with the fluorides of yttrium and of calcium.

SULPHURET OF CERIUM may be obtained, according to Mosander, by passing the vapour of sulphuret of carbon over red-hot carbonate of cerium; or by fusing oxide of cerium with excess of sulphuret of potassium, and removing the soluble parts by washing with water. It is an orange-coloured compound, and appears to consist of

Cerium . . . . 1	..	48	..	75	..	Berzelius.
Sulphur . . . . 1	..	16	..	25	..	74
	<hr/>			<hr/>		26
	1	64		100		100

HYPOSULPHATE OF CERIUM, formed by spontaneous evaporation of a solution of protocarbonate in hyposulphuric acid, crystallizes in delicate colourless prisms containing 42.79 of protoxide *per cent*.

PROTOSULPHATE OF CERIUM may be obtained by digesting the protocarbonate in dilute sulphuric acid: it yields small crystals, of a purplish tint, and difficultly soluble in water.

PERSULPHATE OF CERIUM is a lemon-yellow salt, from which a red-heat expels half the acid, and converts it into a red *subpersulphate*.

PROTOSULPHATE OF CERIUM AND POTASSA. This double salt is obtained when solid sulphate of potassa is added to a solution of a protosalt of cerium: as it dissolves, a white powder falls, which is the potassa-sulphate of cerium, and in this way, by using excess of sulphate of potassa, the whole of the cerium is thrown down: the double salt, though soluble in water, is insoluble in solution of sulphate of potassa. It is deposited from its solution in boiling water in small crystals of a pale amethyst colour. At a red-heat it fuses, but is not decomposed: the alkalis throw down a basic salt from its solution, which can only be perfectly decomposed by long digestion in excess of alkali. This is the most characteristic salt of cerium, and it serves to separate the oxide of cerium, in analytical operations. (Berzelius.)

PHOSPHURET OF CERIUM has not been obtained.

PROTOPHOSPHATE OF CERIUM is an infusible white powder, somewhat soluble in muriatic and nitric acids, but insoluble in excess of phosphoric acid.

CARBURET OF CERIUM is obtained, according to Mosander, by heating the oxalate in a retort.

PROTOCARBONATE OF CERIUM is precipitated by the carbonated alkalis, in the form of a white powder, insoluble in water and in excess of carbonic acid. It is decomposed by a strong heat, and if exposed to air, peroxide of cerium remains, but if air be excluded, the subperoxide (oxyd-oxydul) remains. (Hisinger and Berzelius.) It has been found *native*. When protoxide of cerium is exposed to air it gradually absorbs carbonic acid.

PERCARBONATE OF CERIUM much resembles the protocarbonate in appearance, but it is heavier, and of a less pure white colour.

The remaining combinations of cerium, with the exception of some of its triple salts, have not been examined.

CHARACTERS OF THE SALTS OF CERIUM. The *protosalts* of cerium are colourless, or slightly purple, of a sweet and astringent taste, and bear much general resemblance to the salts of yttrium. They are unaltered by sulphuretted hydrogen, but are precipitated by the hydrosulphuretted alkalis. Ferrocyanuret of potassium occasions in them a white precipitate. The salts of the *peroxide* are of a yellow colour, and the hydrosulphurets occasion in them a white precipitate. None of the other metals precipitate cerium in a metallic state.

Before the blowpipe the oxide of cerium becomes red-brown when ignited. When the proportion is small, it forms with the fluxes a clear, colourless glass, which by increasing the proportion of oxide becomes yellowish-green while hot. With microcosmic salt, if heated a long time in the internal flame, it gives a clear colourless glass. With borax,

under similar circumstances, it gives a faint yellow-green glass while warm, but is colourless when cold. Exposed again for some time to the external flame, it becomes reddish-yellow, which colour it partly retains when cold. If two transparent beads, one of the compound with micro-cosmic salt, the other with borax, be fused together, the triple compound becomes opaque and white.

## § XXII. TELLURIUM.

IN the year 1782, Müller, of Reichenstein, showed that the ores of tellurium contained a peculiar metal, and his opinion was verified by Klaproth in 1798, who named it *Tellurium*, from *tellus*, the earth.

The ores of tellurium are, 1. *Native*, in which the metal is combined with iron and a little gold. 2. *Graphic ore*, which consists of tellurium, gold, and silver. 3. *Yellow ore*, a compound of tellurium, gold, lead, and silver; and 4. *Black ore*, consisting of the same metals with copper and sulphur. These ores have only been found in the Transylvanian mines, and in Siberia.

The metal is extracted from them by precipitating their diluted nitro-muriatic solution by potassa, which is added in excess, so as to redissolve the precipitate: the clear liquor is then poured off, and saturated with muriatic acid, which affords a precipitate of oxide of tellurium. This, heated in a glass retort with charcoal, furnishes the metal, part of which sublimes. Tellurium is of a bright-gray colour, brittle, easily fusible, and volatile. Its specific gravity is 6.1 to 6.3.

OXIDE OF TELLURIUM; TELLUROUS ACID. (*tel + o.*) Exposed to heat and air, tellurium readily burns, exhaling a peculiar odour, which Berzelius ascribes to selenium, and forming a yellowish-white oxide, consisting, according to Klaproth, (*Beiträge*, vol. iii.,) of tellurium 100 + oxygen 20.5. Oxide of tellurium is also obtained by evaporating the nitrate to dryness, and exposing the residue to a dull red-heat. If it be precipitated from its solutions by alkalis, it generally retains a portion of the precipitant.

Dr. Turner adopts, as the result of the latest experiments of Berzelius, the number 64.2 as the equivalent of tellurium, and considers the present oxide as constituted of 1 equivalent of the metal + 2 of oxygen. (*Poggendorff*, xviii., 392.) If it be a protoxide, it will consist of

						Berzelius.	Klaproth.		
Tellurium . . .	1	..	32	..	80	..	80.11	..	83.14
Oxygen . . .	1	..	8	..	20	..	19.89	..	16.86
			<hr/>		<hr/>		<hr/>		<hr/>
	1		40		100		100.00		100.00

PEROXIDE OF TELLURIUM; TELLURIC ACID. When the above oxide is deflagrated with nitre, it is converted, according to Berzelius, into telluric acid: this compound may also be obtained by passing chlorine through the solution of the oxide in potassa till it is fully saturated: slight excess of nitric acid, and a little chloride of barium are then added to separate any accidental traces of sulphuric or of selenic acids; the filtrated liquor is neutralized by ammonia, and chloride of barium added, which occasions a precipitate of *tellurate of baryta*; this, digested with a fourth of its weight of sulphuric acid, (diluted with water), yields a solution which when filtered and carefully evaporated,

yields crystallized *hydrated telluric acid*, from which adhering sulphuric acid may be removed by alcohol. This hydrate loses its water by heat, and the *anhydrous acid*, of a lemon-yellow colour, remains, constituted, according to Berzelius, of

Tellurium . . . .	1	. . .	32	. . .	72.75
Oxygen . . . .	1½	. . .	12	. . .	27.25
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		44		100.00

CHLORIDE OF TELLURIUM is a white fusible compound, formed by heating the metal in chlorine. According to Davy, (*Elements*, p. 410,) it consists of 2 tellurium + 1.85 chlorine; but his experiments were made upon a very limited quantity of materials. The solution of oxide of tellurium in muriatic acid is precipitated as a subsalt by water; excess of water redissolves it. Rose has described a *bichloride*, (Poggendorff, xxi. 443), and according to him, these chlorides form violet vapours, which condense, the one into a black, the other into a white, solid.

IODIDE OF TELLURIUM. Iodine readily combines with tellurium, forming a deep-brown compound, which dissolves in water.

TELLURIUM AND HYDROGEN unite in two proportions: when tellurium is negatively electrized in contact with water, a brown powder is produced, which is the solid *hydruret*: when an alloy of tellurium and tin is acted on by muriatic acid, *telluretted hydrogen gas* is evolved; it reddens litmus, dissolves in water, and possesses the general habitudes of sulphuretted hydrogen; it consists, according to Berzelius, of

1 proportional of tellurium . . . . .	=	32	.	.	.
1     ,,     ,,     hydrogen . . . . .	=	1	.	.	.
		<hr style="width: 50%; margin: 0 auto;"/>			33

in which case, 100 cubical inches must weigh 69.895 grains; its specific gravity, compared with hydrogen, being 33, and with common air 2.91.

SULPHURETS OF TELLURIUM. There appear to be two sulphurets of tellurium, which, according to Berzelius, act as *sulphur-acids*.

THE SALTS OF TELLURIUM are decomposed by the alkalis, and the precipitate is redissolved when they are added in excess. Hydrosulphuret of ammonia forms a brown precipitate; ferrocyanuret of potassium occasions no change. Zinc, lead, tin, copper, cadmium, or iron, immersed into the solutions, cause the separation of metallic tellurium, which generally appears as a black powder.

The oxide of tellurium combines with many of the metallic oxides, acting the part of an acid, and producing a class of compounds which have been called *tellurates*.

TELLURATE OF POTASSA may be formed by heating oxide of tellurium with nitre, and redissolving the residuum in boiling water, which, on cooling, deposits an imperfectly-crystallized white powder, difficultly soluble in water. The tellurates of the alkaline earths, and of many of the metallic oxides, are insoluble\*.

\* The details respecting the properties and composition of the several compounds of tellurium, as given by different chemists, are so much at variance, that I have found it impossible satisfactorily to abridge their results. This is my apology for the imperfect account of this metal given in the text.

## § XXIII. ARSENIC.

THE distinct metallic characters of this substance were first noticed by Brandt, in 1733. Its general chemical relations are such as to place it rather among the simple acidifiable substances than among the metals, for it forms no salifiable base with oxygen, but constitutes *acids*: it, however, has the lustre and opacity of a metal, and conducts electricity. Arsenic may be obtained from the *white arsenic* of commerce, by mixing it with its weight of *black flux*\*, and introducing the mixture into a Florence flask or small retort, placed in a sand-bath, gradually raised to a red-heat: a brilliant metallic sublimate of pure arsenic collects in the upper part of the flask or in the neck of the retort. The volatility of white arsenic prevents its easy reduction by charcoal alone; but the potassa in the flux enables it to acquire a temperature sufficient for its perfect reduction. Arsenic may also be obtained by heating the ore called *native arsenic* (scherbenkobalt of the Germans) in coarse powder in a retort; the metal sublimes, leaving the impurities behind.

Arsenic is of a steel-gray colour, crystalline texture, quite brittle, and of a specific gravity = 5.8. It readily volatilizes, and in close vessels may be sublimed at a temperature of  $360^{\circ}$ , which is lower than its fusing-point. Its vapour has a very strong and peculiarly characteristic smell, much resembling that of garlic. On account of its volatility, its *fusion* is difficultly accomplished, but may be effected by heating it in a sealed tube, under the pressure of its own vapour. Heated in the air, it easily takes fire, burns with a blue flame, and produces copious white fumes of oxide. Exposed to a moist air, or boiled in water, it gradually becomes incrustated with a gray powder, which is an imperfect oxide, or mixture of metallic arsenic and arsenious acid. Berzelius found that, in three months, 100 parts of the metal acquired an increase of about 8.5. This metal and all its compounds are virulent poisons. Its equivalent number is 38. (37.6 Gmelin, 37.7 Turner, 38 Thomson.)

*Native Arsenic* has been found in Saxony, Hanover, France, Bohemia, and Cornwall. It usually occurs in rounded masses, or nodules, of a foliated lamellar texture, in the veins of primitive rocks, and is often associated with silver, cobalt, lead, and nickel ores.

ARSENIC AND OXYGEN. There are two definite compounds of arsenic and oxygen, which are both capable of forming combinations with other metallic oxides. They redden litmus and are soluble in water, and have thence been termed *arsenious* and *arsenic acids*.

ARSENIOUS ACID; WHITE ARSENIC; WHITE OXIDE OF ARSENIC. ( $As + 1\frac{1}{2}O$ .) This is the best known, and most commonly occurring com-

\* This is an extremely useful compound for effecting the reduction of many of the metallic oxides. It consists of charcoal and subcarbonate of potassa, and is best prepared by deflagrating in a crucible a mixture of one part of nitre and two of powdered tartar. The mixture remains in fusion at a red-heat, and thus suffers the small globules of reduced metal to coalesce into a button.

pound of arsenic. It may easily be procured by the combustion of the metal; but as it is formed during certain metallurgic processes, that mode is rarely resorted to. It is abundantly prepared at Joachimsthal in Bohemia, from arsenical cobalt ores, which are roasted in reverberatory furnaces, and the vapours condensed in a long chimney, the contents of which, submitted to a second sublimation, afford the *white arsenic* of commerce. It generally occurs in white, semi-transparent, brittle masses, of a vitreous fracture. Its specific gravity is 3.72. It is nearly tasteless. It generally becomes opaque when long kept, in consequence, apparently, of change in its mechanical texture. It is virulently poisonous, producing a set of peculiar symptoms ultimately followed by inflammation and gangrene of the stomach and intestines: it also proves fatal when applied to a wound; and as the local injury is not sufficient to cause death, it is probable that an induced affection of the nervous system and of the heart is the immediate cause of the mischief. (Brodie's Observations and Experiments on the Action of Poisons, *Phil. Trans.*, 1812, p. 209.) To get rid of the poison by producing copious vomiting and purging, and to pursue the usual means for subduing and preventing inflammation, are the principal points of treatment to be adopted in cases where this poison has been taken. (Orfila, *Traité des Poisons*, tom. i., p. 123.) Upon this, and all other subjects relating to *poisons*, the reader should consult Dr. Christison's excellent treatise.

By a slow sublimation, arsenious acid forms brilliant octoëdral and tetraëdral crystals; and Wöhler has found it in six-sided scales, derived from a rhombic prism. (*Ann. de Chim. et Phys.*, li., 201.) If suddenly heated it runs into a transparent glass, which gradually becomes opaque, whether exposed or not to air; but, according to Dr. Turner, exposure accelerates the change. It is volatile at  $380^{\circ}$ , and *has no smell when perfectly free from metallic arsenic*. (Paris, *Quarterly Journal of Science and Arts*, vol. vi.) According to Klaproth, 1000 parts of water at  $60^{\circ}$ , dissolve from two and a half to three of white arsenic; and 1000 parts of water at  $212^{\circ}$ , dissolve rather more than 77 parts, and about 30 parts are retained in permanent solution. The solutions taste acid and slightly sweet; they redden litmus, but sometimes convert syrup of violets to green. 80 parts of alcohol at  $60^{\circ}$ , dissolve one part of this acid. Its aqueous solution furnishes tetraëdral and octoëdral crystals by slow evaporation, which are anhydrous. It also dissolves in oils. The greater number of the acids merely dissolve white arsenic without forming definite combinations: distilled with an equal weight of dry acetate of potassa, an anhydrous compound of the acetic and arsenic acids passes over, of a most nauseous odour, and so attractive of water as to absorb it rapidly from the air, and with the evolution of so much heat as occasionally to ignite the compound, which burns with a red flame, and exhales arsenious acid. (Berzelius.)

The relative proportions of the components of arsenious acid have been variously stated; but the experiments of Berzelius, corroborated by the results of other analysts, leave little doubt that the oxygen in the arsenious acid is to that in the arsenic acid as 3 to 5; hence, *arsenious acid*, or the *white oxide*, may be considered as composed of

				Thenard.	Davy.	Proust.	Mitscherlich.	Berzelius.
Arsenic	1	. 38	. 76	. 74.24	. 75	. 75.2	. 75.73	. 75.782
Oxygen	$1\frac{1}{2}$	. 12	. 24	. 25.76	. 25	. 24.8	. 24.27	. 24.218
	<u>1</u>	<u>50</u>	<u>100</u>	<u>100.00</u>	<u>100</u>	<u>100.0</u>	<u>100.00</u>	<u>100.000</u>

*Native White Arsenic* occurs in prismatic crystals, and in a pulverulent form: it is found in Saxony and Hungary.

COMBINATIONS OF ARSENIOUS ACID WITH BASES; ARSENITES. These salts, when heated, either evolve arsenious acid or metallic arsenic; in the latter case they are converted into *arseniates*: heated with charcoal metallic arsenic sublimes. The alkaline arsenites, when in solution, are decomposed by lime and the salts of lime, and a white precipitate of *arsenite of lime* falls: they are precipitated green by solutions of copper, and yellow by nitrate of silver. They are not precipitated by sulphuretted hydrogen, except excess of a stronger acid be present; in this way the muriatic solutions of those arsenites which are insoluble in water may also be decomposed.

The *arsenites of ammonia*\*, *potassa*, and *soda*, are easily soluble and uncrystallizable: they are formed by dissolving the acid in the alkaline solutions. Those of *lime*, *baryta*, *strontia*, and *magnesia*, are difficultly soluble, and formed in the same way. *Arsenite of potassa* is the active ingredient in the *liquor arsenicalis* of the *Pharmacopœia*, and in *Fowler's mineral solution* or *tasteless ague-drop*. It produces a white precipitate in the white salts of manganese; a dingy green precipitate in the solutions of iron; a white precipitate in solutions of zinc and tin. Mixed with a solution of sulphate of copper, a precipitate of a fine apple-green colour falls, called from its discoverer, *Scheele's green*, and is useful as a pigment. In the solutions of lead, antimony, and bismuth, it forms white precipitates: added to nitrate of cobalt, it forms a pink precipitate; and bright yellow, with nitrate of uranium. With nitrate of silver it forms a white precipitate, soon becoming yellow, and very soluble in ammonia. All these precipitates are probably *arsenites* of the respective metals, and, heated by a blowpipe on charcoal, they exhale the smell of arsenic. They are decomposed when boiled in solution of carbonate of potassa or of soda: they are soluble in excess of arsenious acid, and easily soluble in nitric acid, and such other acids as form soluble compounds with their bases.

*Native Arsenite of Lead* is found in France, in Spain, and in Siberia.

ARSENIC ACID ( $Ar + 2\frac{1}{2}O$ ) was discovered by Scheele; it is obtained by distilling a mixture of 4 parts of muriatic and 24 of nitric acid off 8 parts of arsenious acid, gradually raising the bottom of the retort to a dull red-heat at the end of the operation. It may also be procured by distilling nitric acid off powdered metallic arsenic.

Arsenic acid is a white substance, of a sour taste; it is anhydrous, deliquescent, and uncrystallizable. Its specific gravity is 3.4. It requires for solution 6 parts of cold and 2 of boiling water; its solution reddens

\* Berzelius has shown that the supposed crystals of arsenite of ammonia deposited by the solution of arsenious acid in ammonia are quite destitute of ammonia, and consist only of arsenious acid.



vegetable blues, and tastes acid and metallic. When water is poured upon it, a part only is immediately dissolved; and another portion, as is the case with phosphoric acid, remains undissolved: after a time, upon agitating the solution, the whole is taken up. Heated to bright redness, it evolves oxygen, and is converted into arsenious acid. If dry arsenic acid be exposed to air, so as gradually to deliquesce, it sometimes forms crystals which are extremely soluble, and are probably *hydrated acid*. Arsenic acid gives a white precipitate with lime-water, and a peculiar reddish-brown with nitrate of silver. It yields a yellow deposit of a sulphuret of arsenic when its solution is subjected to the action of a current of sulphuretted hydrogen gas.

Arsenic acid consists of

				Proust	Mitscherlich.	Berzelius.	Thenard.
Arsenic . . .	1	. 38	. 65.5	. 65	. 65.04	. 65.283	. 65.4
Oxygen . . .	2½	. 20	. 34.5	. 35	. 34.96	. 34.717	. 34.6
	<u>1</u>	<u>58</u>	<u>100.0</u>	<u>100</u>	<u>100.00</u>	<u>100.000</u>	<u>100.0</u>

ARSENIATES are produced by the union of this acid with the metallic oxides; and many which are insoluble may be formed by adding arseniate of potassa to their respective solutions. They are soluble in dilute nitric acid, and in such other acids as do not form insoluble compounds with their bases, and ammonia precipitates them from these solutions. They are readily decomposed by charcoal at a red-heat; but many of them, when heated alone, are unchanged even at a higher temperature. They are decomposed when boiled in solutions of the fixed alkaline carbonates. The soluble arseniates generally give a white precipitate with lime-water: they are not immediately precipitated by solution of sulphuretted hydrogen: protosulphate of iron gives a white precipitate (or yellowish if arsenious acid be at the same time present). With acetate of lead and acetate of zinc they also give white precipitates.

ARSENIATE OF AMMONIA (A + ar') is formed by saturating arsenic acid with ammonia; oblique rhomboidal prisms are obtained on evaporation, which, when gently heated, effloresce and evolve ammonia: at a higher temperature, water is formed, oxide of arsenic sublimes, and nitrogen is evolved, a circumstance first observed by Scheele.

According to Mitscherlich (*Ann. de Chim. et Phys.*, xix.) these crystals very closely resemble those of phosphate of ammonia, and consist of

Ammonia . . .	1	. .	17	. .	19.2
Arsenic acid.	1	. .	58	. .	65.5
Water . . . .	1½	. .	13.5	. .	15.3
	<u>1</u>		<u>88.5</u>		<u>100.0</u>

BINARSENIATE OF AMMONIA is formed by adding to a solution of the above crystals one additional proportional of arsenic acid. On evaporation, crystals resembling those of the biphosphate of ammonia are deposited, containing, according to Mitscherlich,

Ammonia . . . . .	1	. .	17	. .	10.6
Arsenic acid. . . . .	2	. .	116	. .	72.5
Water . . . . .	3	. .	27	. .	16.9
	<u>1</u>		<u>160</u>		<u>100.0</u>

ARSENIATE OF POTASSA ( $P + AR'$ ) when *neutral*, is deliquescent and uncrystallizable.

BINARSENIATE OF POTASSA ( $P + 2 AR'$ ) may either be formed by adding excess of arsenic acid to potassa, and evaporation; or by heating to redness, in a Florence flask, a mixture of equal parts of nitre and white arsenic; during the latter operation much nitrous gas is evolved, and on dissolving the residue in water, filtering, and evaporating, quadrangular crystals of binarsenate of potassa are obtained, resembling those of the biphosphate of potassa: they are soluble in 5.3 parts of water at  $40^\circ$ , and insoluble in alcohol. Macquer was the first who procured this salt; hence termed *Macquer's neutral arsenical salt*. It is not easily decomposed by heat alone, and may be fused and kept red-hot without undergoing other change than losing a little acid, but when mixed with about an eighth of charcoal-powder and distilled, metallic arsenic rises, and carbonate of potassa, mixed with part of the charcoal, remains in the body of the retort. This salt as well as the arsenite, is used for the cure of agues. It is a delicate test of the presence of silver, in solutions of which it occasions a red-brown precipitate: it is also sometimes used to separate iron from manganese; it produces in the persalts of iron a white precipitate, whilst the arseniate of manganese remains in solution. In the crystallized form it consists of

					Thomson.	Mitscherlich.
Potassa	. . . 1	. . . 48	. . . 26.4	. . . 27.074	}	. . . 89.91
Arsenic acid	. . . 2	. . . 116	. . . 63.7	. . . 65.426		
Water	. . . 2	. . . 18	. . . 9.9	. . . 7.500		
	<u>1</u>	<u>182</u>	<u>100.0</u>	<u>100.000</u>		<u>100.00</u>

ARSENIATE OF SODA ( $S + AR'$ ) is formed by saturating a solution of carbonate of soda with arsenic acid; on evaporation, rhombic prisms are obtained, isomorphous according to Mitscherlich, with phosphate of soda: they effloresce in a dry air, and require, according to Thomson, ten parts of water at  $60^\circ$ , for solution, and the liquid has alkaline properties. When dropped into solutions of earthy and metallic salts, this salt occasions precipitates in most of them, a table of which is given by Thomson (*Ann. of Phil.*, xv.) The crystals appear to contain different proportions of water according to the strength of the solution from which they are deposited, and which when concentrated yields them with 8, and when dilute, with 12 equivalents of water: (Marx, über das Verhältniss der Mischung zur Form: Brunswick, 1824,) hence we have them composed of

				Gmelin.			Mitscherlich.
Soda	. . . 1	. . . 32	. . . 19.8	} . 56	. . . 1	. . . 32	. . . 16.2
Arsenic acid	. . . 1	. . . 58	. . . 35.8		. . . 1	. . . 58	. . . 29.3
Water	. . . 8	. . . 72	. . . 44.4		. . . 12	. . . 108	. . . 54.5
	<u>1</u>	<u>162</u>	<u>100.0</u>	<u>100</u>	<u>1</u>	<u>198</u>	<u>100.0</u>
							<u>100.00</u>

BINARSENIATE OF SODA. ( $S + 2 AR'$ .) This salt is formed by adding arsenic acid to a solution of carbonate of soda till the liquid no longer precipitates chloride of barium: on evaporation and exposure to cold, it yields crystals isomorphous with biphosphate of soda, and composed of

	<i>Anhydrous.</i>			Mitscherlich.	<i>Crystallized.</i>			Mitscherlich.
Soda . . .	1	32	21.6	21.631	1	32	17.4	17.36
Arsenic acid	2	116	78.4	78.319	1	116	63.0	62.70
Water . . .					4	36	19.6	19.94
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1	148	100	100.000	1	184	100.0	100.10

ARSENIATE OF LIME (C +  $ar'$ ) is deposited when arsenic acid is dropped into lime-water, or when arseniate of potassa is added to nitrate of lime; it may also be formed by heating a mixture of white arsenic and quicklime, in which case, as Dr. Wollaston first observed, when it has attained a certain temperature, ignition suddenly ensues, and metallic arsenic sublimes; so that one portion of the arsenious acid confers oxygen upon the other, to convert it into arsenic acid. It is soluble in nitric and muriatic acids, and in sulphate, muriate, and nitrate of ammonia: it also dissolves in arsenic acid. *Hydrated arseniate of lime* (Pharmacolite) occurs native, sometimes in fine capillary crystals. Arseniate of lime consists of

	<i>Artificial.</i>			Langier.	<i>Native.</i>			Klaproth.
Lime . . .	1	28	32.6	32.5	1	28	24.75	25.00
Arsenic acid	1	58	67.4	67.5	1	58	51.35	50.54
Water . . .					3	27	23.90	24.46
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1	86	100	100.0	1	113	100.00	100.00

ARSENIATE OF BARYTA. (B +  $ar'$ .) When a solution of arseniate of soda is added, not in excess, to a solution of chloride of barium, a granular precipitate is gradually obtained, which is *neutral* arseniate of baryta; when heated it loses water of crystallization, but is not further decomposed. It consists of

	<i>Anhydrous.</i>			Berzelius.	<i>Crystallized.</i>			Berzelius.
Baryta . . .	1	77	57	57.06	1	77	50.4	50.32
Arsenic acid	1	58	43	42.94	1	58	37.9	37.86
Water . . .					2	18	11.7	11.82
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1	135	100	100.00	1	153	100.0	100.00

SUBSESQUIARSENIATE OF BARYTA. ( $1\frac{1}{2}$  B +  $ar'$ .) When arsenic acid is dropped into baryta-water, or when the neutral arseniate of baryta is digested in ammonia, a white and difficultly-soluble powder is obtained, composed of

			Berzelius.	Langier.
Baryta . . .	$1\frac{1}{2}$	115.5	66.6	65.7
Arsenic acid	1	58.	33.4	34.3
	<hr/>	<hr/>	<hr/>	<hr/>
	1	173.5	100.0	100.0

BINARSENIATE OF BARYTA. (B +  $2ar'$ .) When the neutral arseniate of baryta is dissolved in arsenic acid it yields crystals of the *hydrated binarseniate*: when heated to redness, they leave a compound of

			Mitscherlich.
Baryta . . .	1	77	40.13
Arsenic acid	2	116	59.87
	<hr/>	<hr/>	<hr/>
	1	193	100.00

ARSENIATE OF STRONTIA. (STR +  $ar'$ .) When solutions of nitrate of strontia and arseniate of soda are mixed in atomic proportions, no immediate precipitate appears, but in twenty-four hours small crystals are

formed, which are minute rectangular four-sided prisms, tasteless, not affecting vegetable blues, and very sparingly soluble in water. They contain, according to Dr. Thomson,

Strontia . . . . .	1	..	52	..	28.6
Arsenic acid . . . . .	1	..	58	..	31.8
Water . . . . .	8	..	72	..	39.6
	<hr/>		<hr/>		<hr/>
	1		182		100.0

ARSENIATE OF MAGNESIA ( $M + ar'$ ) is soluble, deliquescent, and uncrystallizable, when there is an excess of acid: but a very difficultly soluble, and *neutral arseniate* may be obtained, partly in powder and partly in tufted crystals, by mixing dilute solutions of sulphate of magnesia and arseniate of soda in atomic proportions, and suffering them to remain at rest for twenty-four hours. The crystals consist, according to Thomson, of 1 atom of anhydrous arseniate of magnesia, and 8 of water; when dried at a temperature of  $500^{\circ}$ , they lose 6 atoms of water, but still retain 2, which are disengaged at a red-heat.

ARSENIATE OF MANGANESE. ( $MAN + ar'$ .) This salt, in a hydrated state, is precipitated in the form of a white powder, when arseniate of potassa is added to chloride of manganese. It is insoluble in water but dissolves in sulphuric and muriatic acids.

PROTARSENIATE OF IRON. ( $FE + ar'$ .) Arseniate of ammonia, added to the solution of protosulphate of iron, occasions a precipitate of *protarseniate* of iron. (Chenevix, *Phil. Trans.*, 1801.) This salt is at first white, but soon acquires a tint of green; it is sparingly soluble in liquid ammonia, and the solution becomes green in the air. According to Berzelius, the mineral called *Skorodite*, found at Graul, near Schwartzenberg, in small blue-green octoëdral crystals, is a *hydrated protarseniate of iron*.

PERARSENIATE OF IRON is an insoluble white powder, which, when heated, loses 17.68 *per cent.* of water, and becomes red: it is soluble in acids, and soluble, when moist, in caustic ammonia. When the neutral protarseniate of iron is digested in nitric acid and evaporated to dryness, or when the solution is precipitated by ammonia, a *subperarseniate* is obtained.

The *Native Cubic Arseniate of Iron*, analyzed by Vauquelin and by Chenevix, is a compound of the hydrated protarseniate and perarseniate. (Berzelius.)

SUBARSENIATE OF ZINC is precipitated in a white gelatinous state, when arsenic acid, or an alkaline arseniate, is added to sulphate of zinc. It is insoluble in water, but soluble in arsenic and in nitric acids.

ARSENIATE OF TIN. A white insoluble powder is precipitated by adding arseniate of potassa to protochloride of tin.

ARSENIATE OF COPPER is formed by adding an alkaline arseniate to nitrate of copper; it is a blue insoluble powder, and when dried at a temperature not exceeding  $212^{\circ}$ , appears to be a *hydrated subperarseniate*.

The *Native Arseniates of Copper* have been submitted to an elaborate investigation by Mr. Chenevix; (*Phil. Trans.*, 1801;) he has described five varieties, as shown in the following table. (Thomson's *System*.)

Variety	1st	2d	3d	4th	5th	Acid.	Oxide.	Water.
	1st	. . .	1.	. . .	3.70	. . .	2.50	
„	2d	. . .	1.	. . .	2.76	. . .	1.	
„	3d	. . .	1.	. . .	1.72	. . .	0.70	
„	4th	. . .	1.	. . .	1.80	. . .	0.53	
„	5th	. . .	1.	. . .	0.88	. . .	0.60	

ARSENIATE OF LEAD. ( $Pl + ar'$ .) This salt is formed when arsenic acid is added to nitrate of lead, or when a solution of nitrate of lead is gradually decomposed by the addition of neutral arseniate of soda. It is white, insoluble in water, but soluble in nitric and muriatic acids, easily fusible, and consists of

				Berzelius.	Thenard.	Chenevix.	
Oxide of lead	. . .	1	. 112	. 65.9	. 65.86	. 64.3	. 63
Arsenic acid	. . .	1	. 58	. 34.1	. 34.14	. 35.7	. 37
		<u>1</u>	<u>170</u>	<u>100.0</u>	<u>100.00</u>	<u>100.0</u>	<u>100.</u>

SUBARSENIATE OF LEAD. When neutral arseniate of soda is added *in excess* to the soluble salts of lead, a white powder falls, composed of

					Berzelius.
Oxide of lead	. . .	1½	. . 168	. . 74.3	. . 74.75
Arsenic acid	. . .	1	. . 58	. . 25.7	. . 25.25
		<u>1</u>	<u>226</u>	<u>100.0</u>	<u>100.00</u>

ARSENIATE OF ANTIMONY. Arseniate of potassa throws down a white precipitate in the muriatic solution of oxide of antimony.

ARSENIATE OF BISMUTH falls in the form of a white powder on adding arsenic acid to nitrate of bismuth; it is insoluble in water, and in nitric acid, but soluble in muriatic acid. (Thenard).

ARSENIATE OF COBALT is precipitated of a red colour by the addition of an alkaline arseniate to a soluble salt of cobalt: it occurs *native* in the *peach-blossom* cobalt.

ARSENIATE OF NICKEL, formed by double decomposition, is an apple-green powder, often granular and crystalline. The mineral called *nickel-ochre* is a *hydrated arseniate of nickel*, composed of 36.20 oxide of nickel, 36.80 arsenic acid, 25.50 water, and a trace of cobalt. (Berthier.)

ARSENIATE OF URANIUM is thrown down of a straw-colour when arseniate of potassa is added to nitrate of uranium.

CHARACTERS OF THE ARSENIATES AND ARSENIATES. These salts are recognised by the alliaceous odour which they exhale when heated in a tube with a little carbonaceous matter, when they also afford a metallic sublimate. The *arsenites*, when heated alone, generally lose part of their acid, which forms a crystallized sublimate; but the *arseniates*, under the same circumstances, retain their acid, unless partially decomposed, as it sometimes is, by the base. The *arsenites*, when dissolved in dilute muriatic acid, and tested by a current, or strong solution of sulphuretted hydrogen, give a yellow cloud of sulphuret of arsenic; but the *arseniates* are not thus decomposed. I have elsewhere adverted (p. 106) to the crystalline analogies between the arseniates and the phosphates, and to the resemblance in the atomic constitution of the phosphoric and arsenic acids.

ARSENIC AND CHLORINE; CHLORIDE OF ARSENIC. ( $Ar + 1\frac{1}{2}C.$ ) This compound may be formed by throwing finely-powdered arsenic into chlorine; the metal burns and produces a whitish deliquescent and volatile compound; it may also be obtained by distilling six parts of corrosive sublimate with one of powdered arsenic; the chloride passes into the receiver in the form of an unctuous fluid, formerly called *butter of arsenic*. A preferable process for obtaining this compound is that of M. Dumas. (*Ann. de Chim. et Phys.*, xxxiii., 360.) One part of arsenious acid with ten parts of sulphuric acid, are put into a tubulated retort, and the temperature raised to about  $212^{\circ}$ . Fragments of fused common salt are then to be thrown in by the tubulature; by continuing the heat, and successively adding the salt, chloride of arsenic is obtained; it distils over, and may be condensed in cold vessels. Very little muriatic acid is disengaged, but towards the end of the operation, a portion of hydrated chloride of arsenic is produced, which floats upon the pure chloride, and appears more viscid and colourless; it may be deprived of water by redistillation with concentrated sulphuric acid. Mixed with a larger quantity of water, the chloride of arsenic is decomposed, and arsenious acid is formed, muriatic acid being at the same time produced.

When sulphur or phosphorus are heated in this chloride they are dissolved, but again deposited on cooling. It combines with oil of turpentine and olive-oil. It absorbs about ten times its volume of chloro-carbonic acid, but gives it off again on dilution with water. Chloride of arsenic consists of

					J. Davy.
Arsenic . . .	1	..	38	..	41.3
Chlorine . . .	$1\frac{1}{2}$	..	54	..	58.7
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		92		100.0
					<hr style="width: 50%; margin: 0 auto;"/>
					100

IODIDE OF ARSENIC, ( $Ar + 1\frac{1}{2}I.$ ) obtained by heating the metal with iodine, is of a deep-red colour, and volatile. When acted upon by water, it produces hydriodic and arsenious acids, whence it appears probable that its composition is analogous to that of the chloride.

It would also appear, from Plisson's experiments (*Ann. de Chim. et Phys.*, xxxix., 266,) that a *periodide* ( $Ar + 2\frac{1}{2}I.$ ) may be formed in the same way.

BROMIDE OF ARSENIC. ( $Ar + 1\frac{1}{2}B.$ ) Bromine and arsenic act intensely on each other with the evolution of heat and light, and form a crystallizable compound which fuses at  $70^{\circ}$ , and boils and evaporates at  $430^{\circ}$ . By the action of water, it yields arsenious and hydrobromic acids. (Serullas, *Ann. de Chim. et Phys.*, xxxviii., 318.)

FLUORIDE OF ARSENIC is obtained by distilling a mixture of 1 part of powdered fluor-spar with 1 of white arsenic and 3 of sulphuric acid. A colourless fuming liquid passes over, which is decomposed by water, and by the contact of glass. Unverdorben, who first examined this compound, states its specific gravity to be 2.73. It is extremely volatile, and fumes in the air. The specific gravity of its vapour exceeds 4. It appears to be a *sesquifluoride*. It combines without decomposition with ammonia.

ARSENIC AND HYDROGEN: ARSENURETTED HYDROGEN GAS. According to Thenard, this gas is best obtained from a powdered alloy, of three parts of tin and one of arsenic, mixed with a portion of powdered arsenic, and acted on by muriatic acid. It may also be obtained by the action of the following alloy upon water. Mix two parts of antimony with two of cream of tartar, and one of white arsenic, and heat the mixture strongly for two hours in a covered crucible. When cold, a button of the triple alloy of potassium, antimony, and arsenic will be obtained, fragments of which may be transferred under a jar inverted in water (*Quarterly Journal*, xiii., 225.) This alloy should be carefully excluded from air and moisture. Soubeiran recommends that an alloy should be obtained by fusing arsenic with its weight of zinc, and that the gas should be procured by the action of this alloy on strong muriatic acid. Great care should be taken to avoid the deleterious effects of this gas; it proved fatal to the late M. Gehlen. (*Ann. de Chim. et Phys.*, iii., 135.)

After standing some time over water, arsenuretted hydrogen deposits a small quantity of brown matter, which appears to be a *hydruret of arsenic*. It is decomposed, and deposits arsenic at high temperatures: exposure to intense cold is said to occasion its liquefaction. It may be kept in dry and well-closed vessels without change. It smells strongly alliaceous; it extinguishes a taper, and burns with a pale-blue flame, depositing arsenic and its oxide. It is sparingly absorbed by water, and has no effect upon vegetable-blue colours. If detonated with oxygen, arsenious acid and water are formed.

If bubbles of chlorine be passed up into a jar of arsenuretted hydrogen, standing over warm water, flame and explosion are often produced, muriatic acid is formed, and a brown hydruret is deposited; but if the gas be passed in the same way by successive bubbles into chlorine, no inflammation results, absorption takes place, and muriatic acid and chloride of arsenic are formed. If the chlorine be not very pure, and when the gases are cold, inflammation seldom follows their mixture. Chlorine, added to a mixture of sulphuretted with arsenuretted hydrogen, causes a deposit of sulphuret of arsenic. Nitric acid suddenly decomposes arsenuretted hydrogen; water, oxide of arsenic, nitrous acid, and nitric oxide are the results. With iodine it yields hydriodic acid and iodide of arsenic. It is decomposed by the action of phosphorus, sulphur, potassium, sodium, and tin, at high temperatures. It is not affected by muriatic, nor phosphoric acids, nor by solutions of the alkaline sulphurets. Many of the metallic oxides and salts decompose it. Corrosive sublimate is a most delicate test of its presence; as soon as it comes in contact with it, calomel is formed, and a metallic film of arsenic and mercury. Bubbles of the gas, passed through a solution of corrosive sublimate, are similarly decomposed. It is not altered by alcohol or ether; the fixed oils absorb it slowly, and acquire a thicker consistency. Oil of turpentine absorbs it, and becomes thick, milky, and sour; and deposits crystals, which, when heated, smell of arsenic and turpentine.

As there is some difficulty in obtaining this gas free from the admixture of hydrogen, the statements respecting its composition and specific gravity, are somewhat at variance. According to Dumas and Soubeiran, (*Ann. de Chim. et Phys.*, xliii.,) the specific gravity of arsenuretted

hydrogen is 2.695; and when decomposed by heat, one volume yields one and a half of hydrogen; when detonated with oxygen, each volume requires one volume and a half for its perfect combustion, water and arsenious acid being the results. It is, therefore, probably composed of one equivalent and a half of hydrogen, and one of arsenic.

HYDRURET OF ARSENIC is a brown compound, obtained by negatively electrifying arsenic in contact with water; or by acting upon water by an alloy of potassium and arsenic. It has not been analyzed. It is not decomposed at a red-heat in nitrogen gas, but in oxygen it burns, and produces water and arsenious acid.

ARSENIC AND SULPHUR: PROTOSULPHURET OF ARSENIC: RED SULPHURET OF ARSENIC: REALGAR. ( $As + S$ .) By slowly fusing a mixture of metallic arsenic and sulphur, or by heating white arsenic with about half its weight of sulphur, a *red sulphuret of arsenic* is obtained. It is crystallizable, and of a vitreous fracture: its specific gravity is 3.4. It may be sublimed, unaltered, in close vessels.

It is usually known under the name of *Realgar*, and occurs *native* in Germany and Switzerland, in veins of primitive rocks and among volcanic matter. Its primitive form is an acute octoëdron. It is used in the preparation of the pyrotechnical compound, called *White Indian Fire*, which consists of 24 parts of saltpetre, 7 of sulphur, and 2 of realgar, finely powdered and well mixed. It burns with a white flame of great brilliancy.

When realgar is digested in a solution of caustic potassa, a part of its sulphur is removed, and a black or brown powder remains, which, when heated, is resolved into realgar and metallic arsenic. Realgar consists of

						<i>Native.</i>	
						Klaproth.	Laugier.
Arsenic . . .	1	..	38	..	70.25	.. 69	.. 69.57
Sulphur . . .	1	..	16	..	29.75	.. 31	.. 30.43
	<hr style="width: 100%;"/>		54		<hr style="width: 100%;"/>	100	<hr style="width: 100%;"/>
	1				100.00		100.00

SESQUISULPHURET OF ARSENIC: YELLOW SULPHURET OF ARSENIC: ORPIMENT. ( $As + 1\frac{1}{2} S$ .) When realgar is fused with sulphur, or when sulphuretted hydrogen is passed through a solution of arsenious acid in dilute muriatic acid, this sulphuret is formed: in the latter case it is in the form of a yellow powder. It is fusible, and assumes a lamellar or crystalline texture on cooling, and may be sublimed without decomposition in close vessels. Heated in the air, it burns with a pale-blue flame, exhaling white fumes and the odour of sulphurous acid. It is soluble in boiling water, and in caustic alkaline solutions: it is insoluble in acids, but is decomposed by nitric and nitromuriatic acids. These sulphurets are readily decomposed by fusion with potassa; sulphuret of potassium and a sublimate of metallic arsenic are the results.

Braconnot has employed an *ammoniacal solution of orpiment* as a dye-stuff, (*Ann. de Chim. et Phys.*, xii.); the process he recommends is as follows: 1 part of sulphur, 2 of white arsenic, and 5 of pearlash, are to be fused in a crucible at a heat a little below redness: a yellow mass results, which is to be dissolved in hot water and filtered; the filtered



solution, diluted with water, is to be treated with weak sulphuric acid, and will give a fine yellow precipitate, which easily dissolves in ammonia, forming a solution at first yellow, but becoming colourless on adding more ammonia. The wool, silk, cotton, or linen, is to be dipped into this solution, more or less diluted according to the colour required, care being taken that no metallic vessels are used; on taking them out they are at first colourless, but, as the ammonia evaporates, become yellow; they are then to be freely exposed to the air, washed, and dried. This colour is very permanent, but soap impairs it. Orpiment is also the basis of the pigment called *King's Yellow*. The composition of orpiment is

								<i>Native.</i>			
						Berzelius.		Laugier.      Klaproth.			
Arsenic	1	..	38	..	61.2	..	61	..	61.86	..	62
Sulphur	$1\frac{1}{2}$	..	24	..	38.8	..	39	..	38.14	..	38
	1		62		100.0		100		100.00		100

*Native Orpiment* (the *auripigmentum* of the ancients) is of a bright lemon or golden colour. It is generally massive and lamellar. It occurs both in primitive and secondary rocks in Suabia, Hungary, China, and South America.

**PERSULPHURET OF ARSENIC.** ( $Ar + 2\frac{1}{2}S$ .) When sulphuretted hydrogen is passed through a concentrated solution of arsenic acid, a yellow precipitate falls, which resembles orpiment in colour, and, like it, may be sublimed without change, in close vessels; it also is easily fusible and soluble in alkaline solutions, but insoluble in boiling water. The same compound is obtained when sulphuretted hydrogen is passed through a concentrated solution of arseniate of potassa, and the resulting sulpho-salt decomposed by muriatic acid. This sulphuret of arsenic\* consists of

								Berzelius.	
Arsenic	. . .	1	..	38	..	48.7	..	48.3	
Sulphur	. . .	$2\frac{1}{2}$	..	40	..	51.3	..	51.7	
		1		78		100.0		100.0	

The sulphurets of arsenic are all poisonous, though less virulent than the oxides. (Orfila.) They combine with sulphur, or are soluble in fused sulphur, in all proportions.

**ARSENIO-SULPHURETS.** Each of the preceding sulphurets of arsenic combines, as a *sulphur-acid*, with the opposed, or electropositive sulphurets, or sulphur-bases, to form a class of *sulphur-salts*, called, by Berzelius, *Arsenio-sulphurets*: hence we have three classes of these salts; namely, the *arsenio-protosulphurets*, the *arsenio-sesquisulphurets*, and the *arsenio-persulphurets*. (*Handbuch*, ii., 447.)

\* According to Berzelius there is a compound of arsenic with a larger relative quantity of sulphur, which is formed when a neutral solution of arsenio-persulphuret of potassium is mixed with alcohol, and filtered; the filtered solution is reduced by distillation to some-  
 what less than half its bulk, and suffered to cool slowly, when it deposits crystalline scales, which are as fusible as sulphur itself, and which he regards as a definite compound of arsenic, with great excess of sulphur. (*Lehrbuch*, ii., 44.)

1. The *arsenio-protosulphurets* (containing realgar, or protosulphuret of arsenic,) are formed, in the dry way, when sulphur-bases are fused with realgar; or when the arsenio-sesquisulphurets are fused with metallic arsenic: when thus obtained, they are decomposed by water, which causes the separation of a black or brown subsulphuret of arsenic, and the residue is an arsenio-sesquisulphuret. These salts cannot be obtained by the direct action of caustic alkali, or of a hydrosulphuret, upon realgar; for in that case, also, an arsenio-sesquisulphuret and black subsulphuret are formed: but they are produced by boiling orpiment in a somewhat concentrated solution of carbonate of potassa, or of soda, and filtering the solution whilst hot; it becomes turbid as it cools, and a brown flocculent precipitate (like Kermes) falls, which is a neutral compound of the alkaline sulphuret with realgar, that is, an *arsenio-protosulphuret of potassium* or of *sodium*. These salts are red or brown, and mostly insoluble in water. The acids decompose them, and separate realgar.

2. The *arsenio-sesquisulphurets* (containing orpiment, or sesquisulphuret of arsenic,) can only be obtained in the dry way, and in a solid state, for when their solutions are evaporated to a certain degree of concentration, a brown powder is deposited (which is an arsenio-protosulphuret,) and an arsenio-sesquisulphuret, with excess of base, remains in solution: but the decomposition is not perfect, till the latter salt crystallizes. By dilution with water, and boiling, the precipitate is redissolved, and the arsenio-sesquisulphuret reproduced. When orpiment is digested in weak caustic alkali at common temperatures, a compound, containing twice the quantity of orpiment that exists in the neutral compound, is obtained. The arsenio-sesquisulphurets of the alkaline bases are not decomposed by dry distillation; the others are decomposed at a red-heat, orpiment is given off, and the sulphur-base remains.

3. *Arsenio-persulphurets*, (containing the persulphuret of arsenic.) These compounds vary in colour; their taste is hepatic, and extremely nauseous and bitter: decomposed by an acid, they give out a very peculiar hepatic odour: when the base is a sulphuret of the metals of the alkalis or alkaline earths, or of glucium or yttrium, or a few of the other metals, these salts are soluble in water; the others are insoluble. These salts are often *basic*, and are then mostly crystallizable, which is rarely the case with the *neutral* compounds: the latter are decomposed by dry distillation, and resolved into arsenio-sesquisulphurets and sulphur; but the basic compounds remain unchanged. They are easily decomposed in the open fire. The concentrated solutions of these salts are only very slowly decomposed by exposure to air; when more dilute, they gradually become turbid, and deposit sulphur and sulphuret of arsenic, whilst the solution contains undecomposed salt, together with arsenites and hyposulphites, which, after complete decomposition, become sulphates\*.

\* Having stated thus much respecting the arsenio-sulphurets, I shall not go into the details of their history, or attempt a description of their manifold varieties; of these the reader may form some notion, by reference to Dr. Turner's abstract of the properties of a few of the leading *arsenio-persulphurets* only, (*Elements of Chem.*, p. 753,) or he may consult Berzelius or Gmelin for a full account of them. The question as to the state of these compounds when in

SULPHURET OF ARSENIC AND IRON is found native in many parts of Europe. It is of a more silvery colour than iron pyrites, and when heated exhales arsenic. It is called *arsenical pyrites*, or *mispickel*. It appears to be a compound of a bisulphuret of iron with binarsenuret of iron; or,

						Chevreul.	Stromeyer.		
Iron . . . . .	2	..	56	..	34.2	..	34.938	..	36.04
Arsenic . . . . .	2	..	76	..	46.4	..	43.418	..	42.88
Sulphur . . . . .	2	..	32	..	19.4	..	20.132	..	21.08
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		164		100.0		98.488		100.00

PHOSPHURET OF ARSENIC is formed by heating the metal, or its oxide, with phosphorus; it is gray and brittle, and requires to be preserved out of the contact of air.

SELENIURET OF ARSENIC is formed by dissolving arsenic in fused selenium: it is a black fusible compound, less volatile than its components, so that excess of either may be driven off by heat. At a red-heat it boils and sublimes.

ALLOYS OF ARSENIC. Arsenic forms alloys with most of the metals, and they are generally brittle and comparatively fusible. With *potassium* it forms a brownish compound, which, when put into water, evolves less hydrogen than pure potassium, in consequence of the formation of hydru-ret of arsenic. With *sodium*, the alloy is either brown and of an earthy aspect, or gray and metallic, according to the proportions of the metals: water acts upon it as upon the former. (Gay Lussac and Thenard, *Recherches Physico-Chimiques*, tom. i.) The alloy of arsenic and *manga-nese* is not known. With *iron*, *zinc*, and *tin*, it forms white brittle com-pounds; with *copper* it forms a white malleable alloy; with *lead*, a brittle compound of a lamellar texture; with *antimony*, the alloy is brittle, hard, and very fusible. It combines with *bismuth*, and probably with *cobalt*, but these alloys have not been examined.

The separation of arsenic from other metals may generally be accom-plished by repeated deflagration with nitre, by which it is acidified, and the arseniate of potassa may afterwards be washed out by hot water; but by some of the metals it is very obstinately retained\*.

aqueous solution, is involved in the same difficulties with that respecting the solu-tions of the sulphurets of the alkaline bases, and admits of similar explanation; as an instance, I transcribe the following table of the composition of the crystal-lized tri-arsenio-persulphuret of sodium, from L. Gmelin.

			Berzelius	
Sulphuret of sodium	3	. 117.9	. 28.89	. 28.47
Tripersulphuret of arsenic	}	2	. 155.2	. 38.03
Water				
	<hr/>	<hr/>	<hr/>	<hr/>
	1	408.1	100.00	100.00

Or,

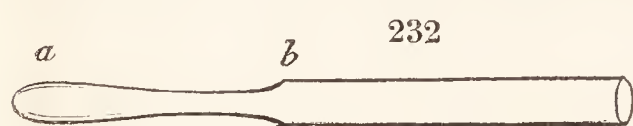
Soda . . . . .	3	. 93.9	. 23.01
Arsenic acid . . . . .	2	. 115.2	. 28.23
Sulphuretted hydrogen	8	. 136.0	. 33.32
Water . . . . .	7	. 63.0	. 15.44
	<hr/>	<hr/>	<hr/>
	1	408.1	100.00

\* When finely-powdered arsenic is boiled in caustic potassa or soda, hydro-gen is evolved, and the metal acidified. When powdered arsenic and caustic hydrate of potassa are heated together, a brown compound is obtained, which appears to be a mixture of arseniuret of potassium and arseniate of potassa. When put into water, it gives out arse-niuretted hydrogen. When the vapour of arsenic is passed over red-hot baryta, a compound is formed, which, however, does not evolve arseniuretted hydrogen when moistened. Heated with carbo-nated alkali, arsenic does not expel the carbonic acid. Heated with fixed oil, arsenic forms a dark plaster of a dis-agreeable odour.

TESTS FOR ARSENIC. As arsenic, either accidentally or intentionally taken, is a very frequent cause of death, and often the subject of judicial inquiry, it becomes of importance to point out the most effectual modes of discovering its presence. Where arsenic proves fatal, it is seldom found in the contents of the stomach after death, but is generally previously voided by vomiting or by stool; and we often can detect it in the matter thrown off the stomach, in the form of a white powder, subsiding in water. The inflammation of the stomach which results is generally a secondary effect, and takes place equally, whether the poison be swallowed or applied to a wound. If minute quantities of white powder be detected, however, in the stomach after death, or in the matter vomited, it is to be carefully collected, and treated as follows:

(a.) Mix a small portion of it with about two parts of black flux; introduce the mixture into a glass tube, and gradually heat it red-hot in the flame of a spirit-lamp. If arsenic be present, a *steel-coloured sublimate* will attach itself to the cooler part of the tube, which, heated in contact of air, evaporates in a *white smoke, strongly smelling of garlic*.

Berzelius recommends the atom of white arsenic to be introduced into the bottom *a* of a tube, shaped as in the margin, and covered up to *b*



with powdered charcoal, previously heated before the blowpipe, to expel all moisture. Heat is then so applied by the flame of a spirit-lamp as to

make the charcoal red-hot; the portion *a* is then heated, and the vapour of the white arsenic is decomposed as it passes through the red-hot charcoal, and a metallic film of arsenic deposited in the cold part of the tube. The bottom of the tube is then cut off, and the arsenic recognised as before, by the alliaceous smell of its vapour.

(b.) Boil the suspected matter in a little distilled water; and when the solution has cooled, add a strong solution of sulphuretted hydrogen, or pass the gas through it. If arsenic be present, a *yellow precipitate* will appear. According to Dr. Ure,  $\frac{1}{100000}$  of arsenious acid may be detected in water by this test. The hydrosulphuretted alkalis do not affect the arsenious solution unless a drop or two of nitric or muriatic acid be added, when the yellow precipitate falls; these tests are, however, equivocal, where very small quantities are to be detected; if a slight excess of alkali be accidentally present, it retains the sulphuret in solution, and excess of acid occasions a little sulphur to fall.

(c.) To the solution *b* add a drop of solution of carbonate of potassa, and then a drop or two of solution of sulphate of copper. An *apple-green precipitate*, commonly known as *Scheele's Green*, indicates arsenic. The ammonio-sulphate and ammonio-acetate of copper also give the peculiar green precipitate when added to very dilute solutions of white arsenic. This test, however, is fallacious when applied to mixed fluids, for Dr. Christison has shown that the ammoniacal solution of sulphate of copper produces in some vegetable and animal infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green; whereas, in other mixed fluids, such as tea and porter, to which arsenic has been added, it occasions none at all if the arsenious acid is small in relative quantity. In some of those liquids a free vegetable acid may be

the solvent, but the arsenite of copper is also dissolved by tannin, and perhaps by other vegetable, as well as some animal principles. (Turner.)

(d.) Add to the solution *b* a drop of nitrate of silver, and of solution of ammonia. A *yellow precipitate* indicates arsenic.

(e.) The Voltaic battery made to act by two wires on a little arsenious solution placed upon a piece of glass, develops metallic arsenic at the negative pole; and if this wire be of copper it becomes whitened.

It must be observed, in regard to these tests, that the first only is unequivocal, and that the appearances produced by the others may originate from the presence of other substances. When, however, all the above appearances ensue, no doubt of the existence of arsenic can be entertained. The several precipitates should be collected, and will, when placed upon a red-hot iron, exhale the peculiar smell of arsenic. The aqueous solution of white arsenic is slowly reduced by zinc, cadmium, and tin, but the addition of a little muriatic acid accelerates the action, and it is then also effected by lead. Arsenic acid is speedily decomposed by zinc, hydrogen being evolved, and the arsenic reduced partly to a metallic state, and partly thrown down as a brown powder (hydruret?) After a time the action ceases, and the solution (of arseniate of zinc) gelatinizes. The decomposition of arsenic acid is also effected in the same way by iron. The reader is referred for further particulars in respect to arsenic as a *poison*, to the means of detecting it, the fallacies of tests, the symptoms it induces, their treatment, and the appearances after death, to the following sources; namely, to Henry's *Elements of Chemistry*; to Murray's *System*; to Dr. Bostock's *Paper* in the *Edinb. Med. and Surg. Journal*, vol. v. p. 166; to Mr. Hume's *Essay*, in the *Phil. Mag.* vol. xxxiii.; and *London Med. and Phys. Journal*, vol. xxiii.; to Dr. Marcet's *Paper* in the *Medico-Chirurgical Transactions*, vol. ii.; to Mr. Sylvester's *Observations* in Nicholson's *Journal*, vol. xxxiii.; to Ure's *Dictionary*—art, ACID (Arsenious); to Orfila's work on *Poisons*; to the *Edinburgh Medical and Surgical Journal* for 1824; to the *Transactions of the Medico-Chirurgical Society of Edinburgh*, vol. ii.; and to the luminous summary of all that relates to the subject, in Dr. Christison's treatise on *Poisons*.

#### § XXIV. MOLYBDENUM.

THE sulphuret is the most common natural compound of this metal: from this ore the *molybdic acid* was first obtained by Scheele in 1778, and from this the metal was obtained by Hielm in 1782. To procure the metal, the native sulphuret is powdered and exposed under a muffle, moderately heated, till converted into a gray powder, which is to be digested in ammonia, and the solution filtered and evaporated to dryness. The residuum is dissolved in nitric acid, re-evaporated to dryness, and violently heated with charcoal. Metallic molybdenum may also be obtained by passing a current of dry hydrogen gas over molybdic acid, strongly heated in a porcelain tube. It should be suffered to cool in the contact of hydrogen.

The metal is of a whitish-gray colour, and of excessively difficult fusion. According to Hielm, its specific gravity is 7.4; according to Bucholz, it

is as high as 8.6, and of the colour of silver, somewhat malleable, and unchanged by air. When exposed to heat and oxygen, molybdenum is acidified, a white crystalline sublimate of *molybdic acid* being formed. At a lower temperature, it first acquires a brown and then a blue film. It is not acted on by dilute sulphuric, muriatic, or hydrofluoric acids; boiled in sulphuric acid, sulphurous acid is evolved, and a brown compound formed: it is dissolved by nitric acid, and very readily by nitromuriatic acid. It is rapidly oxidized by fusion with saltpetre.

Molybdenum forms three compounds with oxygen, two of which are salifiable, and the third, an acid. Its equivalent number is 48, (47.7 Turner; 48 Gmelin.)

PROTOXIDE OF MOLYBDENUM (*mol* + *o*) is obtained, according to Berzelius, by dissolving molybdic acid, or molybdate of potassa or soda in muriatic acid, and putting a piece of pure zinc into the solution; the liquid changes to blue, red and black; excess of ammonia is then added, by which protoxide of molybdenum is thrown down in the form of a *black hydrate*, whilst the oxide of zinc is retained in alkaline solution; the hydrate is then washed, and dried in vacuo over sulphuric acid. It is very apt to retain adhering oxide of zinc. This oxide is difficultly soluble in acids, and the solution, unless very dilute, is almost black; it is insoluble in the caustic alkalis and in the carbonated fixed alkalis; but it is soluble in excess of carbonate of ammonia; when precipitated by that salt from its acid solutions, it consists of

							Berzelius.
Molybdenum . . .	1	..	48	..	85.7	..	85.69
Oxygen . . . . .	1	..	8	..	14.3	..	14.31
	1		56		100.0		100.00

DEUTOXIDE OF MOLYBDENUM; BINOXIDE OF MOLYBDENUM (*mol* +  $2o$ ) was obtained by Bucholz, by strongly heating *molybdate of ammonia* rammed down in a crucible: the molybdic acid is reduced by the hydrogen of the ammonia, and a crystalline copper-coloured substance is obtained, of the specific gravity 5.6. It may also be procured, according to Berzelius, by heating a mixture of muriate of ammonia and molybdate of soda in a platinum crucible till the fumes cease: the residue is well washed, digested in caustic potassa to separate any molybdic acid, and again washed with boiling water. The oxide remains in the form of a black powder, becoming dark-brown when dry, and purple when exposed to the sun's rays. In this state it is almost insoluble in acids and alkalis, and nitric acid converts it into molybdic acid.

The HYDRATED DEUTOXIDE may be obtained by digesting a mixture of molybdic acid and metallic molybdenum in muriatic acid, till the solution, which is at first blue, becomes dark-red: the addition of ammonia then precipitates the hydrate, in colour resembling peroxide of iron. In this state it dissolves in the acids, and forms reddish-brown solutions. It is insoluble in the caustic alkalis, but soluble in their carbonates.

When metallic molybdenum and molybdic acid are boiled together in water, a blue solution is formed, which has sometimes been termed *molybdous acid*, but which appears to be a compound of molybdic acid

with the deutoxide, and consequently a *molybdate of molybdenum*. The deutoxide consists of

				Bucholz.		Berzelius.	
Molybdenum	. 1 . .	48 . .	75 . .	73 . .	75 . .		
Oxygen	. . . 2 . .	16 . .	25 . .	27 . .	25 . .		
	—	—	—	—	—		
	1	64	100	100	100.		

PEROXIDE OF MOLYBDENUM, OR MOLYBDIC ACID. (*mol* + 3 *o*) or *mol'*. To obtain this acid, the native sulphuret of molybdenum should be triturated, to reduce it, as far as possible, to powder, and distilled, with three or four parts of nitric acid, to dryness. This operation should be repeated, till the ore is converted into an uniform white mass, which consists of molybdic, nitric, and sulphuric acids; the two latter may be expelled by a red-heat, in a platinum crucible, and the remaining molybdic acid repeatedly washed with boiling-water, in which it is little soluble, will be nearly pure. It may be rendered perfectly pure by solution in ammonia, precipitation by nitric acid, and exposure to heat. Molybdic acid may also be procured by roasting the powdered native sulphuret at a low red-heat, till it ceases to give out sulphurous acid; the residue, by digestion in ammonia, affords a *molybdate of ammonia*, which may be purified by crystallization, and decomposed by a moderate heat in a platinum crucible, so as to leave the molybdic acid.

The molybdic acid, thus procured, is a white powder, of the specific gravity of 3.46, and requiring, according to Hatchett, 960 parts of boiling water for its solution, which is yellow, reddens litmus, but has no sour taste. Its solubility probably differs with its aggregation, for Bucholz found it soluble in about 500 parts of cold water. Heated to redness in an open vessel, it slowly sublimes, and condenses in brilliant yellowish scales. It dissolves in hot sulphuric acid, forming a solution, which is colourless while hot, but on cooling acquires a blue colour, which is heightened by the addition of soda. Its muriatic solution is pale yellowish-green, but becomes blue when saturated by potassa. (Hatchett, *Phil. Trans.*, 1796.)

It dissolves in the alkalis forming solutions which are colourless, and from which the molybdic acid is at first precipitated, but afterwards dissolved, by the stronger acids. Molybdic acid is composed of

				Berzelius.		Bucholz.	
Molybdenum	. 1 . .	48 . .	66.7 . .	66.613 . .	67.5 . .		
Oxygen	. . . 3 . .	24 . .	33.3 . .	33.387 . .	32.5 . .		
	—	—	—	—	—		
	1	72	100.0	100.000	100.0		

MOLYBDATE OF AMMONIA. (*mol'* + A.) This salt is obtained by dissolving molybdic acid in excess of ammonia, and leaving it to spontaneous crystallization; it forms square prisms, of a pungent metallic taste. When the ammoniacal solution is boiled down, it affords, on cooling, a crystalline mass of *bimolybdate* of ammonia; which, by spontaneous evaporation, may be obtained in rhombic crystals of a pale blueish-green colour, and difficultly soluble in water. Distilled in close vessels this salt yields water, ammonia, and nitrogen, and leaves brown deutoxide; in open vessels the residue is molybdic acid. (Berzelius).

MOLYBDATE OF POTASSA ( $mol' + P$ ) is formed by digesting the acid in potassa; or by heating to redness two parts of nitre with one of molybdic acid, and lixiviating the mass. Its solution, which is colourless, yields small rhomboidal crystals by evaporation, and affords a precipitate of molybdic acid, to muriatic, nitric, and sulphuric acids. When chlorine is passed through it, a white powder falls, difficult of solution in cold water, but instantly dissolved by hot, which Berzelius suspects to be a *bimolybdate of potassa*.

MOLYBDATE OF SODA ( $mol' + S$ ) is more soluble than molybdate of potassa, and furnishes permanent and transparent crystals. In obtaining this salt, a deposit of a yellowish powder ensues, which is probably a *bimolybdate of soda*.

MOLYBDATE OF LIME ( $mol' + C$ ) is thrown down in the form of an insoluble powder, when alkaline molybdates are added to solutions of lime.

MOLYBDATE OF BARYTA ( $mol' + B$ ) falls in the form of a flocculent precipitate, which collects into crystalline grains, when molybdate of ammonia is added to a solution of nitrate of baryta: by heat it acquires a blue tint. It dissolves in nitric and muriatic acids, and these solutions deposit it, when evaporated, in the form of a crystallized rind.

MOLYBDATE OF STRONTIA ( $mol' + STR$ ) is insoluble in water.

MOLYBDATE OF MAGNESIA ( $mol' + M$ ) is soluble in water, and forms clusters of small prismatic crystals, which become yellow when heated, and lose 28 *per cent.* of water: it dissolves in 12 to 15 times its weight of water (Berzelius).

MOLYBDATE OF MANGANESE ( $mol' + MAN$ ) is a white and somewhat soluble powder.

MOLYBDATE OF PROTOXIDE OF IRON is insoluble, and of a dark-brown colour (Scheele).

MOLYBDATE OF PEROXIDE OF IRON is a yellowish-brown precipitate, decomposed by caustic alkali.

MOLYBDATE OF ZINC is insoluble in water, white, pulverulent, and soluble in the stronger acids.

MOLYBDATE OF PEROXIDE OF TIN is a gray powder, insoluble in water, soluble in caustic potassa and in muriatic acid, but not altered by muriatic acid.

MOLYBDATE OF COBALT is precipitated of a dirty-yellow colour, but becomes red by drying: it is decomposed by the alkalis and by the stronger acids.

MOLYBDATE OF NICKEL is a pale-green powder, soluble in boiling water.

MOLYBDATE OF LEAD. ( $mol' + PL.$ ) This compound is precipitated in the form of an insoluble powder: it dissolves in nitric acid and in caustic alkalis; it occurs *native*, crystallized, and of different shades of yellow. It was first discovered in Carinthia, and has since been found in Mexico, Hungary, and Saxony: it was analyzed by Mr. Hatchett, (*Phil. Trans.*, 1796, p. 323,) whose researches have thrown much light upon the nature of the molybdic compounds.

It consists of



				Native.		Artificial.
				Hatchett.	Göbel.	Berzelius.
Oxide of lead . . . .	1	112	60.87	60.4	59.5	64.42
Molybdic acid . . . .	1	72	39.13	39.6	40.5	35.58
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1	184	100.00	100.0	100.0	100.00

MOLYBDATE OF COPPER is yellow-green, difficultly soluble in water, and easily decomposed by acids and alkalis.

MOLYBDATE OF URANIUM is a pale-yellow powder, soluble in the stronger acids and in carbonate of ammonia.

CHLORIDES OF MOLYBDENUM. According to Berzelius there are three chlorides of molybdenum corresponding in composition to the oxides.

PROTOCHLORIDE OF MOLYBDENUM ( $mol + c$ ) is obtained by dissolving the protoxide, to saturation, in muriatic acid; the solution is of a very deep red-brown colour, and leaves on evaporation a viscid mass, soluble in water. It forms double salts with muriate of ammonia, and with chloride of potassium.

BICHLORIDE OF MOLYBDENUM. ( $mol + 2c$ .) This compound is formed by heating metallic molybdenum in pure and dry chlorine; the metal burns, and a very dark-red vapour fills the retort, which condenses into crystals much resembling iodine; they are fusible, volatile, and in the air first fume a little, and then deliquesce into a black liquid, which changes colour in proportion to the water it absorbs, becoming blue-green, green-yellow, dark-red, rose-coloured, and lastly, yellow. When the crystals are thrown into water, much heat is evolved; if the solution be dilute, it becomes green or blue in consequence of oxidizement. This chloride forms a triple ammonio-chloride of molybdenum, with muriate of ammonia.

PERCHLORIDE OF MOLYBDENUM ( $mol + 3c$ ) is formed when molybdic acid is dissolved in muriatic acid: it is obtained in the solid form, when a current of chlorine is passed over gently-heated deutoxide of molybdenum. A white or yellowish crystalline sublimate is formed, and molybdic acid remains in the tube: this compound is less volatile than the bichloride, but it rises in vapour at a temperature below redness: it does not fuse. It readily dissolves in water, and is soluble in alcohol: its taste is sharp, astringent, and afterwards, sour.

IODIDES OF MOLYBDENUM. Iodine has no action on metallic molybdenum at any temperature. *Protiodide of Molybdenum* ( $mol + i$ ) may be formed by dissolving the protoxide in hydriodic acid. *Biniodide of Molybdenum* ( $mol + 2i$ ) is produced when the deutoxide is dissolved in hydriodic acid; the solution yields dark-red crystals on evaporation.

BROMIDE OF MOLYBDENUM has not been examined.

PROTOFLUORIDE OF MOLYBDENUM ( $mol + f$ ) is formed by dissolving the hydrated protoxide in hydrofluoric acid; a dark-purple solution is obtained, which, by very careful evaporation, leaves a purple viscid residue; at a higher temperature it becomes brown, and loses its perfect solubility in water: it forms triple compounds with ammonia, and with the fluorides of potassium and sodium.

BIFLUORIDE OF MOLYBDENUM ( $mol + 2f$ ) is obtained by saturating hydrofluoric acid with the deutoxide: on evaporation a black crystalline

compound is obtained, which yields a red aqueous solution: it forms double salts with ammonia, potassium, and sodium.

PERFLUORIDE OF MOLYBDENUM ( $mol + 3f$ ) is the result of the solution of molybdic acid in hydrofluoric acid; it yields, on evaporation, a yellow uncrystallizable residue, which easily acquires a blue tinge from dust, or other reducing agents.

MOLYBDENUM AND SULPHUR. There are three *sulphurets of molybdenum*, two of which correspond with the deutoxide and with molybdic acid; and the third contains 4 equivalents of sulphur: no *protosulphuret*, corresponding with the protoxide, has as yet been formed.

BISULPHURET OF MOLYBDENUM ( $mol + 2S$ ) is produced artificially by intensely heating a mixture of molybdic acid and sulphur, out of the contact of air. It forms the *native sulphuret*, and consists of

					Bucholz.	Brandes.	
Molybdenum . . . .	1	..	48	..	60	..	59.6
Sulphur . . . . .	2	..	32	..	40	..	40.4
	<hr/>		<hr/>		<hr/>		<hr/>
	1		80		100		100.0

*Native Sulphuret of Molybdenum* is found in Bohemia, Sweden, and near Mont Blanc, disseminated in a gray granite. It has been found in England, chiefly in Cornwall; and in Scotland, in Inverness-shire. It rarely occurs crystallized; generally massive, and in easily-separable laminae. It is soft and unctuous to the touch, and in colour much like lead; infusible, and unchanged by heat when air is excluded. Its properties have already been referred to, as a source of molybdenum. It is found exclusively in primitive rocks; generally in granite, and with quartz.

TERSULPHURET OF MOLYBDENUM ( $mol + 3S$ ) is obtained by saturating a strong solution of a molybdic salt with sulphuretted hydrogen, and then adding muriatic acid; a dark-brown precipitate falls, which becomes black on drying, and which, when heated in close vessels, gives off sulphur, and becomes bisulphuret: it dissolves slowly in the caustic alkalis, and more easily in the alkaline hydrosulphurets.

It consists of

					Berzelius.		
Molybdenum . . . .	1	..	48	..	50	..	49.72
Sulphur . . . . .	3	..	48	..	50	..	50.28
	<hr/>		<hr/>		<hr/>		<hr/>
	1		96		100		100.00

This sulphuret combines with the sulphurets of the electropositive metals (alkaline bases), and forms a class of *sulphur-salts*, which may be called *molybdo-tersulphurets*.

MOLYBDO-TERSULPHURET OF POTASSIUM. ( $mol + 3S$ ) + ( $po + S$ )  
This salt is formed by saturating molybdate of potassa by sulphuretted hydrogen, and evaporating; it forms prismatic crystals of a beautiful green and iridescent lustre; by transmitted light they are ruby-red, soluble in water, and insoluble in alcohol; on the addition of the stronger acids, sulphuretted hydrogen is evolved, tersulphuret of molybdenum is precipitated, and a salt of potassa remains in solution. This salt is anhydrous, and consists of

						Berzelius.
Sulphuret of potassium	1	..	56	..	36.8	.. 35.57
Tersulphuret of molybdenum	1	..	96	..	63.2	.. 64.43
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>		<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	1		152		100.0	100.00

Similar soluble *molybdo-tersulphurets* may be formed with sulphurets of sodium, and lithium, and with those of barium, strontium, and calcium; and several insoluble *molybdo-tersulphurets* are obtained by double decomposition.

**PERSULPHURET OF MOLYBDENUM; QUADROSULPHURET OF MOLYBDENUM.** (*mol* + 4 *S*.) This compound is obtained as follows: saturate bimolybdate of potassa with sulphuretted hydrogen, and boil the resulting turbid solution for some hours in a retort; when it cools, a black light powder, and red crystalline scales are deposited, which must be separated as far as possible; the red crystalline deposit is then washed upon a filter with water, till the washings no longer afford a *red* (not a brown) precipitate with muriatic acid; the residue upon the filter is then treated by boiling water, and the dark-red solution which filters through is decomposed by excess of muriatic acid; a bulky dark-red or brown precipitate falls, which is the quadrosulphuret; it is washed and dried, during which it shrinks, acquiring a gray lustre, and giving a cinnamon-brown powder. It consists of

						Berzelius.
Molybdenum	1	..	48	..	42.86	.. 42.58
Sulphur	4	..	64	..	57.14	.. 57.42
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>		<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	1		112		100.00	100.00

This, like the tersulphuret, combines with the protosulphurets of the electropositive metals, and forms *molybdo-persulphurets*; they are rarely crystallizable, and of a red or orange colour.

**SALTS OF THE OXIDES OF MOLYBDENUM.** There are three classes of these salts: those of the *protoxide*; of the *deutoxide*; and of *molybdic acid*.

1. The salts of the *protoxide* are black or deep purple; they have a purely astringent taste. 2. The salts of the *deutoxide*, when anhydrous, are nearly black, but red when they contain water of crystallization: their solutions have an astringent, sourish, and metallic taste; they are rendered brown by infusion of galls, and a gray-brown precipitate falls; ferrocyanuret of potassium occasions a dark-brown precipitate, which is insoluble in excess of the precipitant. They are rendered black by an immersed plate of zinc, and a black zinciferous protoxide of molybdenum falls. 3. The *molybdic acid*, before it has been heated, is soluble in the other acids, and produces a class of compounds which, in some of their characters, resemble the common salts; but they combine with the alkalis in the manner of a double acid.

There is also a class of molybdic compounds of a deep-blue colour; they are double salts, the basis of which is a compound of the deutoxide with molybdic acid.

Before the blowpipe molybdic acid melts by itself upon the charcoal with ebullition, and is absorbed. In a platinum spoon it emits white fumes, and is reduced in the interior flame to molybdous acid, which is blue, but in the exterior flame it is again oxidated and becomes white.

With microcosmic salt, in the exterior flame, a small proportion of the acid gives a green glass, which by gradual additions of the acid passes through yellow-green to reddish, brownish, and hyacinth-brown, with a slight tinge of green. In the interior flame the colour passes from yellow-green, through yellow-brown, and brown-red, to black; and if the proportion of acid be large, it acquires a metallic lustre, like the sulphuret, which sometimes remains after the glass has cooled. Molybdic acid is but sparingly dissolved by borax. In the exterior flame the glass acquires a gray-yellow colour. In the interior flame black particles are precipitated from the clear glass, leaving it almost colourless when the quantity of molybdenum is small, and blackish when the proportion is large. If, to a glass formed of this acid and microcosmic salt, a little borax be added, and the mixture fused in the exterior flame, the colour becomes instantly reddish-brown: in the interior flame the black particles are also separated, but in smaller quantity. By long-continued heat the colour of the glass is diminished, and it appears yellower by the light of a lamp than by daylight. This acid is not reduced by soda in the interior flame.

### § XXV. CHROMIUM.

CHROMIUM was discovered by Vauquelin in 1797. It was named from *χρῶμα*, *colour*, on account of its tendency to produce coloured compounds. Its two native combinations are the *chromate of lead*, in which the metal was originally discovered, (*Ann. de Chimie.*, xxv. and lxx.) and the *chromate of iron*, which is a compound of the oxides of chromium and iron, found abundantly at Unst in Shetland, and in several parts of Europe and America. Metallic chromium may be obtained by intensely igniting its *oxide* with charcoal. Its colour resembles that of iron; its specific gravity is 5.9. It is brittle, and difficult of fusion, and has only been imperfectly examined in its metallic state. It is said by Bucholz, to be feebly attracted by the magnet; it is not easily acted on by acids. Its equivalent is 28.

CHROMIUM AND OXYGEN. There are two well-defined oxides of chromium: the *protoxide*, which is a salifiable base; and the *peroxide*, or *chromic acid*. According to Berzelius, there also exists a definite *deutoxide*.

PROTOXIDE OF CHROMIUM; SESQUIOXIDE OF CHROMIUM. (*chr* +  $1\frac{1}{2}$  *o*.) There are several modes of obtaining this oxide:—1. When metallic chromium is exposed to the action of heat and air, it combines superficially with oxygen, and this oxide is formed. 2. The simplest method of obtaining it consists in heating *chromate of mercury* red-hot. 3. It may be obtained by calcining a mixture of equal parts of *chromate of potassa* and sulphur in a close earthen crucible, at a red-heat, and washing the green mass which is produced, to dissolve out the sulphate and sulphuret of potassa: the oxide of chromium remains, and is rendered pure by repeated washings. (*Ann. de Chim. et Phys.*, xiv., 299.) 4. By digesting chromate of lead in a mixture of muriatic acid and alcohol; an ether is formed, chloride of lead thrown down, and chloride of chromium remains in solution; it may be precipitated in the state of

*carbonate of chromium* by carbonate of potassa, and this precipitate washed, and heated red-hot, yields the pure protoxide. 5. Chromate of potassa may be dissolved in excess of muriatic acid, and sulphuretted hydrogen passed through the solution, which reduces the chromic acid to oxide, the muriatic solution of which may be decomposed as above.

Protoxide of chromium is of a green colour, infusible and unchanged by heat. After exposure to a red-heat it is scarcely attacked by the acids, but readily dissolves in them when recently precipitated, and in the state of hydrate. It is converted into *chromic acid* by deflagration with nitre. Fused with vitrifiable substances, and especially with borax, it confers upon them a characteristic green colour: hence its use in porcelain and enamel painting. It is the colouring-matter of the emerald.

When it is precipitated from its acid solutions, by the caustic fixed alkalis, it falls in the form of a bulky green powder, soluble in excess of the alkali, but again thrown down on boiling the solution: in this state it is a *hydrate*. It is very sparingly dissolved by excess of ammonia. It may be best obtained by adding a mixture of equal parts of muriatic acid and alcohol, in small portions, to a boiling solution of chromate of potassa, until the liquid acquires a pure green colour. When cold, excess of ammonia is added, which precipitates the oxide, combined with a large relative proportion of water; and in this state it readily dissolves in the acids. (Thomson.)

When tartaric acid is added to the aqueous solution of *chromate of potassa*, it causes an effervescence, and the solution becomes green in consequence of the conversion of the chromic acid into protoxide of chrome: the addition of ammonia now throws down a bulky green tasteless powder, readily soluble in acids, which is also an hydrated oxide of chromium; when heated, it loses as much as thirteen-fifteenths of its weight of water, leaving two-fifteenths of dry protoxide, of a green colour, but difficultly soluble. According to Thomson, this therefore contains a larger quantity of water than any other metallic hydrate.

Berzelius states, that when oxide of chromium, obtained by gently drying the hydrate, is heated nearly red-hot in a crucible, it suddenly becomes ignited throughout, without either gaining or losing weight: this occurs in close as well as in open vessels; when cool it has a fine green colour, and has become insoluble in the acids. To render it again soluble it must be digested in concentrated sulphuric acid, or fused with caustic potassa, or with nitre. In this respect it resembles zircon and titan acid. As oxide of chromium is generally obtained by heating the chromate of mercury red-hot, it most commonly is in the insoluble state; when its solutions are required, they are best obtained from the *hydrate*. This oxide consists of

Chromium	. . . 1	. . . 28	. . . 70	. . . 70.11
Oxygen	. . . 1½	. . . 12	. . . 30	. . . 29.89
	<hr/>	<hr/>	<hr/>	<hr/>
	1	40	100	100.00

*Native Protoxide of Chromium* has been found in France, in the department of the Rhone, in the form of a green incrustation. It is the colouring-matter of the emerald, and exists in a few other minerals.

DEUTOXIDE OF CHROMIUM. When nitrate of chromium is decom-

posed at a red-heat, an insoluble *brown deutoxide* is formed. When heated with muriatic acid, chlorine is evolved, and a muriate, containing the protoxide, is formed. According to Berzelius, when a solution of chromic acid in sulphuric acid, is digested with the hydrated protoxide of chromium, a brown solution is obtained, from which the deutoxide, in the state of hydrate, is precipitated by the caustic alkalis: he says that it dissolves in, and gives distinct salts with, the acids; distinguished from the protosalts by their brown colour, and convertible into protosalts by deoxidizing agents. At a red-heat this deutoxide loses oxygen, and becomes protoxide. According to Döbereiner, this oxide may be regarded as a *dichromate of chromium*: or a compound of two atoms of the green oxide and one of chromic acid.

CHROMIC ACID: PEROXIDE OF CHROMIUM. ( $chr + 3O$ ) or *chr'*. Pure chromic acid may be procured, according to Unverdorben, by the following process, from the ore called *chromate of iron*, which is a more common mineral than the chromate of lead. It is a compound of the oxides of iron and chromium. Reduce it to a fine powder, and expose it to a bright red-heat for two hours, mixed with half its weight of nitre; wash the contents of the crucible, and add to the lixivium nitric acid sufficient to neutralize the excess of potassa: in this way a solution of nitrate and of chromate of potassa is obtained. Upon adding nitrate of lead to this solution, *chromate of lead* is precipitated in the form of a yellow powder, which is to be washed, dried, and heated to redness. Of this chromate, four parts are then well mixed with three of finely-powdered and pure fluor-spar (previously heated red-hot), and five of concentrated sulphuric acid; this mixture is introduced into a distillatory apparatus of lead or platinum, and gently heated; a red vapour is liberated, which is conducted into distilled water contained in a vessel of platinum: it is thus condensed into a dark orange-coloured liquid: the red vapour is a *fluoride of chromium*, and is resolved by water into hydrofluoric and chromic acids, the solution of which, evaporated in a platinum vessel, leaves pure chromic acid. If, instead of conducting the vapour into water, it be received into a platinum vessel, containing pieces of moist blotting-paper, it is decomposed as before; but the chromic acid is deposited in beautiful acicular crystals, which soon deliquesce.

“Another method of preparing chromic acid has been suggested by M. Arnold Maus, which consists in decomposing a hot concentrated solution of bichromate of potassa by silicated hydrofluoric acid: the chromic acid, after being separated from the sparingly-soluble fluoride of silicium and potassium, is evaporated to dryness in a platinum capsule, and then redissolved in the smallest possible quantity of water: by this means the last portions of the double salt are rendered insoluble, and the pure chromic acid may be separated by decantation. The acid must not be filtered in this concentrated state, as it then corrodes paper like sulphuric acid, and is converted into chromate of the green oxide of chromium. When it is wished to prepare a large quantity of chromic acid by this process, porcelain vessels may be safely employed in the first part of the operation, provided care is taken to add a quantity of silicated hydrofluoric acid, not quite sufficient for precipitating the whole of the potassa.” (Turner's *Elements*.)

Chromic acid was formerly obtained by decomposing chromate of lead, or chromate of baryta, by sulphuric acid; but in that case, when the solution is evaporated, the crystals which are obtained always retain sulphuric acid, and if it be attempted to expel this by heat, part of the chromic acid is itself decomposed. (Gay Lussac, *Ann. de Chim. et Phys.*, xvi., 102.)

Chromic acid is of a dark-red colour, becoming almost black when heated; its taste is sour and metallic; it tinges the cuticle yellow; it may be obtained from its aqueous solutions in deliquescent prismatic crystals, of a ruby colour. When heated red-hot, it gives out a portion of oxygen, and becomes the green protoxide; it is energetically acted on and converted into oxide by ammonia. It dissolves in alcohol, and the solution gradually deposits green oxide. It combines with sulphuric acid, and the compound forms octoëdral crystals, formerly mistaken for pure chromic acid. With muriatic acid it forms a compound which dissolves gold. The aqueous solution of chromic acid is decomposed by the sun's rays, and deposits the oxide. Chromic acid appears to be the colouring matter of the ruby.

The salts of chromic acid are said to be isomorphous with those of the sulphuric and selenic acids. It is composed of

							Berzelius.
Chromium . . .	1	. . .	28	. . .	53.85	. . .	53.98
Oxygen . . .	3	. . .	24	. . .	46.15	. . .	46.02
	1		52		100.00		100.00

CHROMATE OF AMMONIA ( $chr' + A$ ) is formed by saturating ammonia with chromic acid, and concentrating the solution over sulphuric acid in vacuo; it forms yellow crystalline scales, having an alkaline reaction, very soluble, and anhydrous. (Thomson.)

BICHROMATE OF AMMONIA ( $2chr' + A$ ) is produced when the solution of the preceding salt is concentrated on a sand-heat; it forms crystalline plates, resulting from an oblique rhombic prism (Brooke, *Ann. of Phil.*, 2nd series, vi., 287), and which include 2 atoms of water. (Thomson.)

CHROMATE OF POTASSA. ( $chr' + P$ .) This salt is prepared by exposing a mixture of 4 parts of powdered native chromite of iron with 1 of nitre, to a strong heat for some hours, and washing out the resulting soluble matter; the process is repeated till the ore is decomposed. The washings yield *chromate of potassa* by evaporation: it forms yellow crystals, the primary form of which is a right rhombic prism (Brooke, *Ann. of Phil.*, 2nd series, vi., 120). It has a disagreeable metallic taste. It is extremely soluble in boiling-water. At 60°, 100 parts of water dissolve about 48 of the salt. It is insoluble in alcohol. Its specific gravity is 2.6. According to Thomson it is anhydrous, and its colouring power is so great, that one part imparts colour to 40,000 of water. If one grain be dissolved with 20 of nitre, and the solution evaporated, the crystals of nitre are almost as yellow as those of the chromate. When heated to redness it acquires a crimson colour, but becomes again yellow on cooling. When fused, it becomes green from loss of oxygen (*Ann. of Phil.*, xvi., 321). Heated with acetic acid and alcohol it is converted into acetate

of potassa, and acetate of protoxide of chromium (Tassaert, *Ann. de Chim. et Phys.*, xxii., 51). It consists of

				Tassaert. Thomson.
Potassa	. . . . 1	. .	48	. . 48
Chromic acid	. . 1	. .	52	. . 52
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	1		100	100.

BICHROMATE OF POTASSA ( $2chr' + P$ ) is obtained by adding a sufficiency of sulphuric acid to a solution of the chromate to give it a sour taste, and setting it aside for a day or two, when deep orange-coloured or red crystals are deposited. It is also produced by mixing the aqueous solution of the chromate with nitric acid. It yields splendid crystals in the form of quadrangular prisms and tables, which are permanent in the air, of a cooling metallic taste, and soluble in 10 parts of water at  $60^{\circ}$ . Their specific gravity is 1.98. At a red-heat they melt, without decomposition, into a transparent red liquid. This salt is largely manufactured at Glasgow, for the use of calico-printers. It consists of

				Grouvelle.	Thomson.	Tassaert.
Potassa	. . . 1	. 48	. 31.5	. 31.154	. 31.579	. 32.6
Chromic acid	. 2	. 104	. 68.5	. 68.846	. 68.421	. 67.4
	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	1	152	100.0	100.000	100.000	100.0

BICHROMATE OF CHLORIDE OF POTASSIUM. When 2 atoms of chromic acid and 1 of chloride of potassium are dissolved in muriatic acid, crystals may be obtained from the solution, which are in the form of flat quadrangular prisms, having the colour of the bichromate of potassa. The same salt is formed when a mixed solution of bichromate of potassa and muriatic acid is boiled; in that case the requisite chloride of potassium is formed at the expense of the muriatic acid and potassa. This salt is permanent in the air, and may be dissolved without decomposition in dilute muriatic acid; but, by pure water it is again resolved into muriatic acid and bichromate of potassa. In this compound, therefore, the chloride of potassium acts as a *base* to the chromic acid. Peligot has obtained similar bichromates of the chlorides of sodium, calcium, magnesium, and ammonium (*Ann. de Chim. et Phys.*, lii., 267). The chloro-bichromate of potassium consists of

						Peligot.
Chromic acid	. . . 2	. .	104	. .	57.7	. . 58.21
Chloride of potassium	1	. .	76	. .	42.3	. . 41.29
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>		<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	1		180		100.0	99.50

CHROMATE OF SODA ( $chr' + S$ ) crystallizes in oblique rhombic prisms, efflorescent in dry air (Brooke, *Ann. of Phil.*, 2nd series, vi., 287), and of a fine yellow colour, very soluble in water, and sparingly so in alcohol: they consist of 1 atom of anhydrous chromate + 12 atoms of water. The *bichromate of soda* is red, and forms large irregular plates, consisting of 1 atom of anhydrous bichromate + 20 atoms of water. (Thomson.)

CHROMATE OF LITHIA ( $chr' + L$ ) forms yellow oblique prisms very soluble in water. (C. Gmelin.)



CHROMATE OF LIME. (*chr'* + C.) When chromate of potassa is mixed with solution of chloride of calcium a yellow precipitate gradually falls: the salt described by Vauquelin as forming silky crystals, is probably a *bichromate of lime*.

CHROMATE OF BARYTA (*chr'* + B) is a pale-yellow powder which falls when chromate of potassa is dropped into chloride of barium: it is very sparingly soluble in water, but soluble in nitric and muriatic acid, and in excess of chromic acid, and again precipitable by ammonia. (Gmelin.) It consists of

				Vauquelin.	Berzelius.				
Baryta . . . . .	1	..	77	..	59.4	..	57.75	..	59.85
Chromic acid . . . . .	1	..	52	..	40.6	..	42.25	..	40.15
	1		129		100.0		100.00		100.00

CHROMATE OF STRONTIA. (*chr'* + STR.) An insoluble pale-yellow powder: it dissolves in nitric, muriatic, and chromic acids (Gmelin).

CHROMATE OF MAGNESIA (*chr'* + M) may be formed by dissolving magnesia in chromic acid; it forms transparent rhomboidal crystals, very soluble in water, and containing 1 atom of anhydrous chromate + 2 atoms of water. (Thomson.)

CHROMATE OF MANGANESE. Neither chromate nor bichromate of potassa produce any immediate precipitate in solutions of the protoxide of manganese, but after a time a brown precipitate falls: the chromic acid appears to be partially deoxidized by the oxide of manganese.

CHROMATE OF IRON. No combination of the protoxide of iron with chromic acid can exist, because it abstracts oxygen from that acid, and produces oxide of chromium. The chromate of the peroxide of iron (*perchromate*) is soluble; and there is a brown insoluble subchromate. The compound called *native chromate of iron*, is a compound of oxide of chrome with protoxide of iron: its specific gravity is 4.6. It sometimes forms octoëdral crystals: it is not soluble in the dilute acids, but may be decomposed by fusion with potassa, or with nitre.

CHROMATE OF ZINC. Chromate of potassa throws down a yellow flocculent precipitate in solution of sulphate of zinc, soluble in excess of the latter salt, and sparingly so, according to Moser, in water.

CHROMATE OF TIN. Protoxide of tin decomposes chromic acid. *Perchromate of tin* is thrown down as a yellow precipitate when permuriate of tin is mixed with chromate of potassa.

CHROMATE OF CADMIUM has not been described.

CHROMATE OF COBALT is a gray insoluble powder.

CHROMATE OF NICKEL is a red deliquescent salt; the alkalis throw down from it a *subchromate* of an orange colour.

CHROMATE OF COPPER. When chromate of potassa and sulphate of copper are mixed, a buff-coloured precipitate falls: it is soluble in ammonia, with a fine green colour.

CHROMATE OF LEAD. (*chr'* + PL.) When chromate of potassa is added to any of the soluble salts of lead, a fine yellow powder falls, which is the neutral chromate: it is insoluble in water, but soluble in nitric acid, and in solution of potassa: solution of carbonate of potassa forms with it carbonate of lead and chromate of potassa: muriatic acid forms

with it chloride of lead, and a muriatic solution of chromic acid: when heated its colour is deepened, and it fuses at a red-heat (Vauquelin). A diluted solution of nitrate of lead being added to a very alkaline solution of chromate of potassa, and left at rest for some time, there was found in the mixed solution, small red crystals, which, upon examination, proved to resemble in all their characters the native chromate of lead. (Faraday.)

*Native Chromate of Lead* is of a deep orange-red colour; when pulverized, orange-yellow. It occurs crystallized in many varieties of form, of which the *primitive* is, according to Haiüy, an oblique prism: it is somewhat translucent and brittle. Specific gravity 6. Before the blow-pipe it crackles, and melts into a greyish slag. It occurs in the gold mine of Beresof, in Siberia, in a vein traversing gneiss and mica slate; and near the same place in fissures in a sandstone. (W. Phillips.) Chromate of lead is anhydrous, and consists of

				Pfaff.		Berzelius.	
				<i>Native.</i>		<i>Native</i> <i>Artificial.</i>	
Oxide of lead	. . . 1	. 112	. 68.29	. 67.91	. 68.38	. 68.147	
Chromic acid	. . . 1	. 52	. 31.71	. 31.72	. 31.62	. 31.853	
	<hr/>	1	164	100.00	99.63	100.00	100.000

DICHROMATE OF LEAD; SUBCHROMATE OF LEAD ( $chr' + 2Pl$ ). This salt was first noticed by Dulong and Grouvelle, in 1812 and 1822, and its composition pointed out by Badams in 1825 (*Ann. of Phil.*, 2nd series, ix., 303). It is formed by digesting the neutral chromate in caustic potassa; or by boiling a mixture of the neutral chromate with two thirds its weight of oxide of lead, in water: it is an insoluble scarlet-coloured powder, which, when digested in acetic acid, loses half its oxide. Liebig and Wöhler prepare it by adding the neutral chromate to fused nitre, and washing the residue (Poggend., xxi., 580). It is anhydrous, and consists of

						Badams.	
Oxide of lead	. 2	. . 224	. . 81.16	. . 80.98			
Chromic acid	. 1	. . 52	. . 18.84	. . 19.02			
	<hr/>	1	276	100.00	100.00		

These chromates of lead are valuable pigments, and used both in oil and water colours, in calico printing, and dyeing (Lassaigne, *Ann. de Chim. et Phys.*, xv., 76).

CHROMATE OF ANTIMONY. Chromate of potassa added to a muriatic solution of oxide of antimony forms a brown precipitate, soluble with a green colour, in excess of the antimonial solution.

CHROMATE OF BISMUTH is formed by mixing chromate of potassa with nitrate of bismuth; it is a lemon-coloured powder, very sparingly soluble in water, and reddened by solution of potassa. (Grouvelle.)

CHROMATE OF URANIUM. Chromate of potassa occasions an ochre-yellow precipitate in solution of nitrate of uranium. (Moser.) Carbonate of uranium dissolved by chromic acid yields small cubic and dendritic crystals. (John.)

CHROMATE OF MOLYBDENUM. When chromic and molybdic acids are dissolved in boiling-water, they form a yellow solution, which yields on

evaporation an uncrystallizable residue, with which water forms a brown solution, and leaves a yellow and difficultly-soluble powder. (Berzelius.)

CHROMATES OF MERCURY, SILVER, &c. (See those metals.)

CHLORIDE OF CHROMIUM; SESQUICHLORIDE OF CHROMIUM ( $chr + 1\frac{1}{2}c$ ). This compound is obtained by red-heating a mixture of dry protoxide of chromium and charcoal in a current of dry chlorine: a pink crystalline sublimate gradually rises, soft to the touch, and transparent when in thin layers. It slowly dissolves in water, and yields a green solution similar to that obtained by dissolving the hydrated protoxide of chrome in muriatic acid; or by decomposing chromate of lead by muriatic acid mixed with a little alcohol. When this aqueous solution of the chloride is evaporated, a dark-green *hydrated chloride* remains (composed of 2 atoms of sesquichloride and 3 water), and when this is heated to about  $500^{\circ}$  out of the contact of air, it again becomes anhydrous: in this state it consists of

Chromium . . .	1	. .	28	. .	34.2
Chlorine . . .	$1\frac{1}{2}$	. .	54	. .	65.8
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		82		100.0

PERCHLORIDE OF CHROMIUM; TERCHLORIDE OF CHROMIUM ( $chr + 3c$ ). This compound may be obtained by distilling a mixture of chromate of lead, chloride of sodium, and sulphuric acid, and conducting the evolved vapour, which is a mixture of chlorine, muriatic acid, and terchloride of chromium, through a tube cooled to  $0^{\circ}$ , by which the latter is condensed into a dark-red liquid, heavier than water, very volatile, and exhaling fumes in the air, of the colour of nitrous acid. It acts violently on water, and produces a muriatic solution of chromic acid: it absorbs chlorine and dissolves iodine. A small fragment of phosphorus brought into contact with a drop of this compound, inflames and explodes; it is also rapidly decomposed by sulphur and by mercury\*, (Dumas and Berzelius). It probably consists of

Chromium . . .	1	. .	28	. .	20.6
Chlorine . . .	3	. .	108	. .	79.4
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		136		100.0

Neither the *iodide* nor the *bromide of chromium* have been examined.

FLUORIDE OF CHROMIUM. When protoxide of chromium is dissolved in hydrofluoric acid, and evaporated to dryness, a green crystallized salt remains, soluble in water. It forms difficultly-soluble double salts with the fluorides of ammonium, potassium, and sodium.

PERFLUORIDE OF CHROMIUM; TERFLUORIDE OF CHROMIUM ( $chr + 3f$ ). This compound was discovered by Unverdorben in 1824 (Trommdorf's *Journal der Pharmacie*, ix., and *Edin. Journal of Science*, iv.) He obtained it by the process above described, under the head of *chromic acid*, and is the red vapour there mentioned (p. 768). In consequence of its powerful action on glass, the gas can only be collected and preserved

\* This seems to be the compound which Dr. Thomson described under the name of *chlorochromic acid*: he states that dry phosphorus has no action on it, but that the slightest adhering moisture causes explosion. Unverdorben is stated by Dumas to have obtained the above compound.

in vessels of platinum, so that its properties have been but imperfectly studied: it explodes when mixed with ammonia, and it seems doubtful whether it forms compounds with that gas, analogous to the fluoboric and fluosilicic acids. The action of water on this compound has been above adverted to: it appears to be composed of

Chromium . . .	1	..	28	..	34.1
Fluorine . . .	3	..	54	..	65.9
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		82		100.0

Hence, when decomposed by the action of water, 1 atom of this fluoride is resolved into 1 atom of chromic acid ( $chr + 3O$ ), and 3 atoms of hydrofluoric acid ( $3h + f$ ).

**NITRATE OF CHROMIUM.** When hydrated protoxide of chromium is dissolved in nitric acid, the solution is blue by reflected, but red by transmitted light: evaporated to dryness, a red deliquescent uncrystallizable salt (deutonnitrate of chromium) remains. A solution of chromic acid in nitric acid yields on evaporation dark brownish-red granular crystals.

**SULPHURET OF CHROMIUM** is formed by passing the vapour of sulphuret of carbon through a red-hot porcelain tube, containing protoxide of chromium; or by heating a mixture of hydrated protoxide and sulphur, in vacuo: it is of a dark-gray colour, and when heated in the air it burns into oxide, evolving sulphurous acid: nitromuriatic acid converts it into a sulphate of the protochloride of chromium. It is insoluble in potassa and in hydrosulphuret of potassa. It consists of

Chromium . . .	1	..	28	..	53.85	..	54
Sulphur . . .	$1\frac{1}{2}$	..	24	..	46.15	..	46
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		52		100.00		100.

Rose and  
Berzelius.

This sulphuret is a weak *sulphur base*, and forms a few sulphur salts.

**SULPHITE OF CHROMIUM.** Sulphurous acid readily dissolves the hydrated protoxide.

**SULPHATE OF CHROMIUM.** When the solution of hydrated protoxide of chromium in dilute sulphuric acid is evaporated, an insoluble *subsalt* remains.

**AMMONIA-SULPHATE OF CHROMIUM.** This salt forms purple octoëdral crystals. (Haidinger, *Edin. Jour. of Science*, i. 100.)

**POTASSA-SULPHATE OF CHROMIUM.** When a mixed solution of acid protosulphate of chromium, and sulphate of potassa, is left to spontaneous evaporation, regular octoedra crystals, appearing purple in one direction, and green in another, are deposited. When this salt is dissolved in water, and the solution evaporated, it can only be again obtained in regular crystals, when excess of sulphuric acid is present, by which the solubility of the salt is diminished. This salt, Berzelius observes, may be called *chrome alum*, and if aluminum were substituted for chromium, common alum would be the result; so that there are not less than four isomorphous oxides which give aluminoid salts with potassa and sulphuric acid,

namely, those of aluminum, manganese, iron, and chromium. It consists of

				Berzelius.
Potassa . . . . .	1	..	48	.. 9.38
Protoxide of Chromium . . . . .	2	..	80	.. 15.90
Sulphuric acid . . . . .	4	..	160	.. 31.80
Water . . . . .	24	..	216	.. 42.92
	<hr/>		<hr/>	<hr/>
	1		504	100.00

**CHROMOSULPHATE OF POTASSA.** When solutions of chromate and of sulphate of potassa are mixed and evaporated, a double salt is obtained, containing 43.3 of chromate and 56.7 of sulphate of potassa: it forms pale yellow prismatic crystals, and yields a precipitate with nitrate of baryta, which is only partially soluble in nitric acid. It has occasionally been substituted for chromate of potassa. It has a bitterish taste and is readily soluble in cold and hot-water. (Boutron Charlard, *Journal de Pharm.*, ix., 184.)

**PHOSPHURET OF CHROMIUM.** When phosphate of chromium is intensely heated with charecoal a gray phosphuret is obtained. When phosphuretted hydrogen gas is passed over sesquichloride of chromium at a red-heat, a black phosphuret is the result, which burns before the blowpipe, and is insoluble in muriatic acid. (Rose.)

**PHOSPHATE OF CHROMIUM.** When phosphate of potassa is added to a solution of protochloride of chromium a gray precipitate falls. The solution of hydrated protoxide of chromium in phosphoric acid is emerald green and uncrystallizable. (Vauquelin.)

**CARBONATE OF CHROMIUM.** The gray-green precipitate which the carbonated alkalies produce in solutions of the protosalts of chromium, is not a true carbonate, but a compound of subcarbonate and hydrate of protoxide of chromium. (Berzelius). It dissolves, according to Meissner, in solution of carbonate of potassa, forming a grass-green liquid. It is sparingly soluble in carbonate of ammonia.

None of the *alloys of chromium* are important, nor have they been much examined.

Before the blowpipe, the oxide of chromium exhibits the following properties: it is fusible with microcosmic salt in the interior flame, into a glass which at the instant of its removal from the flame is of a violet hue, approaching more or less to dark blue or red, according to the proportion of the chromium. After cooling, the glass is bluish-green, but less blue than copper glass. In the exterior flame the colour becomes brighter, and less blue than the former. With borax it forms a bright-yellowish or yellow-red glass in the exterior flame; and in the interior flame this becomes darker and greener, or bluish-green.

## § XXVI. VANADIUM.

THIS metal was discovered by Sefström in the year 1830; its name is derived from *Vanadis*, a Scandinavian deity; he found it in the ores of iron from Taberg in Sweden, and in the slags from the reducing furnaces. The same metal was shortly after found by Mr. Johnston of Durham, in a lead ore from Wanlock-head; and by Del Rio, in a lead ore from Zemapan

in Mexico: the latter terms it *Erythronium*, from the red colour of its acid. Thus have three persons noticed the existence of Vanadium without the knowledge of each other's labours, but the merit of being the first discoverer is fairly due to Professor Seftström. (*Phil. Mag. and Ann.* x. 321; *Ann. de Chim. et Phys.*, xlvii., 377; Brewster's *Journal*, v. 318, new series; Poggendorff's *Ann.* xxii. 1.)

Vanadium is most readily obtained from the native *vanadate of lead*, by the following process of Mr. Johnston; the ore is dissolved in nitric acid, and a current of sulphuretted hydrogen passed through the solution, by which lead and arsenic are precipitated, and a blue solution obtained, which is evaporated to dryness: the residue is dissolved in ammonia, and a piece of sal ammoniac larger than it can dissolve is introduced into the solution: *Vanadate of ammonia* then subsides in the form of a white powder, which should be washed, first with a solution of muriate of ammonia (in which it is insoluble) and then with alcohol of the specific gravity 0.86. This salt may be decomposed by heating and stirring it in a platinum crucible till it acquires a red colour; it is then *vanadic acid*. Berzelius succeeded in reducing this acid by the action of potassium, which at a moderate heat suddenly decomposes it, and on washing the residue, vanadium remains in a pulverulent form. Vanadium may also be obtained by decomposing the liquid chloride of vanadium by a current of dry ammonia, and heating the white saline mass which is so produced.

Vanadium has somewhat of a silvery lustre, is extremely brittle, conducts electricity, and is not acted upon by air or water at common temperatures; at a dull red-heat it takes fire and burns into a black oxide; it is not acted upon by sulphuric, muriatic, or hydrofluoric acids, but nitric and nitromuriatic acid yield dark blue solutions: it is not acted on by boiling caustic potassa, or by the alkaline carbonates at a red-heat; its equivalent is 68. (68.5 Turner.)

VANADIUM AND OXYGEN. There are three compounds of this metal with oxygen; two oxides, and an acid.

PROTOXIDE OF VANADIUM. ( $Va + O$ ). When a stream of dry hydrogen gas is passed over heated vanadic acid, water is formed, in consequence of the partial reduction of the acid, and a black substance remains, which is extremely infusible, conducts electricity, is strongly electronegative in relation to zinc, and which, when heated in the air, is converted by slow combustion into the deutoxide. It is not salifiable. From these characters, this substance, if not vanadium, would appear to be a mixture of the metal with a portion of the oxide: according to Berzelius it is a compound of 68 vanadium + 8 oxygen, and therefore a *protoxide*. Exposed to air and moisture it slowly absorbs oxygen, and when kept in water gradually communicates to it a green tint: the same change occurs in alkaline and acid solutions, and with the exception of nitric and nitromuriatic acids, it is not dissolved by them.

DEUTOXIDE OF VANADIUM. ( $Va + 2O$ ). When 10 parts of protoxide and 12 of vanadic acid are intimately mixed and heated in an exhausted vessel, or in one filled with carbonic acid, a black compound is obtained, which is insoluble in water, and which consists of 68 vanadium + 16 oxygen. This is the only salifiable oxide: it may be obtained in the state

of *hydrate*, by precipitation from its acid solutions by carbonate of soda, and if carefully dried out of the contact of air is of a gray colour, and gives out its water when heated. In this hydrated state it yields blue solutions with the acids: it also dissolves in caustic potassa and in ammonia, forming brown liquids.

**VANADIC ACID.** ( $Va + 3O$ ). When vanadate of ammonia is moderately heated and stirred in an open vessel, it gradually acquires a red colour, and leaves vanadic acid: heated in a close vessel, the hydrogen of the ammonia deoxidizes the acid, and the deutoxide is the product: vanadic acid when fused, is red; but when in powder, brown: it fuses at a heat below redness, and in the act of crystallizing, as it cools, it contracts in bulk and gives out so much latent heat as to become incandescent. It undergoes no change by heat, provided all deoxidizing agents are excluded; when any combustible matter is present it passes into the state of oxide: it is tasteless; insoluble in alcohol, and nearly so in water. The equivalent of vanadic acid is 92: it consists of

Vanadium . . . . .	1	..	68	..	74
Oxygen . . . . .	3	..	24	..	26
	1		92		100

**VANADIATES.** The compounds of vanadic acid with salifiable bases are generally orange-coloured or yellow, but they sometimes are produced colourless, without any apparent change of composition: it forms neutral and bi-salts, those with the alkalis being soluble, and with the other oxides, either sparingly soluble or insoluble. The soluble salts are easily deoxidized, by alcohol, sulphuretted hydrogen, sulphurous acid, and several of the hydracids. Vanadic acid dissolves and forms variously coloured compounds with the deutoxide of vanadium: these compounds are formed when the deutoxide in water is exposed to air; it gradually forms vanadic acid, and the solution becomes blue, green, yellow, and red, according to the extent of acidification. It also combines with some of the other acids, as is the case with the chromic acid.

The colour of vanadic acid distinguishes it from others, with the exception of the chromic, with which it was at first confounded; but the *blue* colours, as opposed to the green of chromic acid, produced by deoxidizing substances, is a distinctive character. When heated with borax before the blowpipe it produces, like chromic acid, a green bead in the reducing flame; but in the exterior flame, the green remains if from chrome, but becomes yellow if from vanadium.

**SALTS OF VANADIUM.** The salts of the deutoxide of this metal are best obtained by the action of the respective acids upon the hydrated deutoxide: they are blue, and afford a gray precipitate with the alkalis, which when exposed to air becomes red: infusion of galls blackens them. The *nitrate of vanadium*, which is at first blue, becomes red during evaporation, from the formation of vanadic acid.

**CHLORIDES OF VANADIUM.** When deutoxide of vanadium is digested in muriatic acid a brown compound is obtained, which appears to be a *bichloride*. ( $Va + 2C$ ). When dry chlorine is passed over a red-heated mixture of protoxide of vanadium and charcoal, in a glass or porcelain tube, a yellow liquid is obtained, which when acted upon by water yields

muriatic and vanadic acids; it is therefore a *terchloride* ( $Va + 3C$ ). By the action of hydriodic, hydrobromic, hydrofluoric, and hydrocyanic acids upon the oxide, an *iodide*, *bromide*, *fluoride*, and *cyanuret* of vanadium may be obtained.

**SULPHURETS OF VANADIUM.** By passing a current of sulphuretted hydrogen over the deutoxide heated to redness, a *bisulphuret of vanadium* is ultimately obtained. The same compound is formed when sulphate of ammonia is mixed with a solution of a salt of vanadium, till the precipitate first formed is redissolved, and then, decomposing the deep purple solution by sulphuric or muriatic acid: a brown bisulphuret subsides, which becomes black when it is dried. In the hydrated state it is dissolved by the alkalies and alkaline sulphurets, but is insoluble in the acids, with the exception of the nitric and nitromuriatic, by which it is converted into sulphate. When sulphuretted hydrogen is passed through vanadic acid in water, a mixture of hydrated deutoxide and sulphur is precipitated; but when a solution of vanadic acid in hydrosulphuret of ammonia is acidulated by muriatic or sulphuric acid, a hydrated *tersulphuret* subsides; its colour is at first light brown, but it becomes almost black by drying, and heated to redness in close vessels, it gives off water and sulphur, and is resolved into the bisulphuret. It dissolves in alkalies and in alkaline sulphurets.

**PHOSPHURET OF VANADIUM.** When phosphate of vanadium mixed with a little sugar is exposed to a white-heat, a gray phosphuret is obtained. (Turner's *Elements*, 577, *et seq.*)

## § XXVII. TUNGSTEN.

THIS metal, which has also been called *Scheelium* and *Wolframium*, was first obtained by Messrs. de Luyart, from the *tungstic acid* previously discovered by Scheele, in 1781\*. It is obtained by exposing a mixture of tungstic acid and charcoal to a red-heat; or by passing hydrogen over the ignited acid. It is very difficult of fusion, very hard, brittle, and of an iron colour. Its specific gravity 17.4. By the action of heat and air, tungsten is converted into an oxide, which is of a yellow colour. It is also oxidized by nitric acid. It is gradually dissolved by solution of potassa, with the evolution of hydrogen, and a tungstate of potassa is produced. The equivalent of tungsten may be assumed at about 100. (96 Gmelin, 99.7 Turner.)

**OXIDE OF TUNGSTEN; DEUTOXIDE OF TUNGSTEN** ( $tu + 2O$ ) may be obtained by mixing finely-powdered wolfram with twice its weight of carbonate of potassa, and fusing it in a platinum crucible. Tungstate of potassa is thus formed, which is dissolved in hot-water, with half its

\* There are two native combinations or *ores* of tungsten, which are resorted to as sources of the metal: these are *Wolfram* and *Tungstate of Lime*.

*Wolfram* is found in primitive countries, generally accompanying tin ores; its colour is brownish-black: it occurs massive and crystallized, its primitive form being a rectangular parallelepiped.

It abounds in Cornwall. It consists of tungstic acid, united with oxides of iron and manganese.—Thomson's *Annals*, vi. 198.

*Native Tungstate of Lime* is a whitish semitransparent substance, found in England, Saxony, Bohemia, and Sweden, and occurring crystallized and massive. Its most usual form is the octoëdron.



weight of muriate of ammonia, evaporated to dryness, and heated red-hot in a Hessian crucible. The mass is then well washed in boiling water, and digested in weak solution of potassa. The residue is oxide of tungsten. In this process the tungstate of potassa and muriate of ammonia form chloride of potassium and tungstate of ammonia; but at a red-heat the ammonia decomposes the tungstic acid, and reduces it to the state of oxide, which is prevented by the fused chloride of potassium from passing into the state of acid. (Wöhler, *Quarterly Journal*, xx., 177.) Thus prepared, the oxide is black, and when heated to redness, it suddenly ignites, and becomes converted into tungstic acid by the absorption of oxygen. It does not appear capable of entering into combination with the acids so as to form salts. When a current of hydrogen gas is carefully passed over heated tungstic acid, it is partially deoxydized and converted into a chocolate-coloured oxide, which neither combines with acids nor with bases, and which is identical in composition with the above. (*Ann. de Chim. et Phys.*, xvii., 16.) If the action of hydrogen be too long continued, the oxide itself is reduced. This oxide consists of

				Berzelius.
Tungsten . . . . .	1	100	86.25	85.54
Oxygen . . . . .	2	16	13.75	14.46
	1	116	100.00	100.00

Wöhler has described an interesting combination of this oxide with soda, which is obtained by adding as much tungstic acid to fused tungstate of soda as it will dissolve, and then passing hydrogen over the compound at a red-heat: on washing out the undecomposed tungstate with water, a golden-coloured substance remains, in small cubes and scales of a metallic lustre, and insoluble in caustic alkalies and in nitric, sulphuric, and nitro-muriatic acids, but soluble in hydrofluoric acid. At a red-heat, oxygen, chlorine, and sulphur decompose it. It cannot be obtained by the direct combination of soda with the oxide. (*Poggend.*, ii., 345.) It consists of

				Wöhler.
Soda . . . . .	1	32	12	12.4
Oxide of Tungsten. . . . .	2	232	88	87.6
	1	264	100	100.0

TUNGSTIC ACID ( $tu + 3 O$ ) or  $tu'$ , is obtained when the oxide is heated red-hot and stirred, in an open vessel. When finely-powdered native tungstate of lime is boiled for some hours in nitric acid, tungstic acid is separated, in the form of a yellow powder, which may be freed from adhering nitric acid, by dissolving it in ammonia, and heating the tungstate of ammonia to redness. Tungstate of potassa, prepared by heating wolfram with carbonate of potassa, as above described, may also be decomposed by nitric acid, and the precipitate heated with ammonia as before.

Tungstic acid is a yellowish powder, which appears green whilst hot, and also acquires a greenish colour by long exposure to the sun's rays. Its specific gravity is 6.12. It is insoluble in water, but readily soluble in the caustic alkalis. When precipitated by the acids from its ammo-

niacal solution, a portion of the precipitant is carried down with it, and in this way compounds of sulphuric, nitric, and muriatic acids, with tungstic acid, may be produced, which are more or less soluble in water.

When tungstic acid is exposed to a heat of about  $600^{\circ}$  in a current of hydrogen, it becomes blue; a similar product is obtained when metallic zinc is put into a mixture of muriatic and tungstic acids; or when tungstate of ammonia is decomposed by distillation in a retort. This has sometimes been regarded as a distinct oxide, but, according to Berzelius, it is a tungstate of the oxide, or a compound of the acid and oxide. Tungstic acid consists of

				De Luyart.	Buchholz.	Berzelius.			
Tungsten . . .	1	..	100	..	80.64	..	80	..	79.766
Oxygen . . .	3	..	24	..	19.36	..	20	..	20.234
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	1		124		100.00		100		100.000

**GENERAL PROPERTIES OF THE TUNGSTATES.** The alkaline and earthy tungstates are colourless; they are heavy; and those which are soluble have a bitter metallic taste: muriatic, nitric, and sulphuric acids occasion in them white precipitates. When their acid solutions are acted upon by zinc, they acquire the blue colour above adverted to.

**TUNGSTATE OF AMMONIA** is procured in crystalline scales, sparingly soluble in water, of a metallic taste, by digesting the acid in ammonia. It contains, according to Berzelius,

					Berzelius.
Ammonia . . . .	1	..	17	..	6.338
Tungstic acid . . .	2	..	248	..	87.000
Water . . . . .	2	..	18	..	6.662
	<hr/>		<hr/>		<hr/>
	1		283		100.000

**TUNGSTATE OF POTASSA** is uncrystallizable and deliquescent. The acids occasion precipitates in its solution, which are triple compounds of tungstic acid, potassa, and the acid used as a precipitant. The *Nitro-tungstate of Potassa* is the salt originally described by Scheele as tungstic acid. It dissolves in 20 parts of water, at  $212^{\circ}$ , and reddens litmus.

**TUNGSTATE OF SODA** crystallizes in hexaëdral tables, soluble in 4 of cold, and 2 parts of boiling water, and of an acrid taste. Sulphuric, nitric, and muriatic acids occasion precipitates, as in the tungstate of potassa.

**TUNGSTATE OF LIME, OF BARYTA, and OF STRONTIA,** are insoluble white compounds.

**TUNGSTATE OF MAGNESIA** is obtained by boiling the acid with magnesia, filtering, and evaporating; it crystallizes in pearly scales. The acids produce precipitates of triple compounds in its solution.

**TUNGSTATE OF MANGANESE,** formed by adding tungstate of potassa to muriate of manganese, is an insoluble white powder. (John, *Gehlen's Journal*, iv.) *Tungstate of Iron* is also insoluble: *Tungstate of Zinc* and of *Tin* have not been described, nor have any of the remaining tungstates been examined in their pure state.

**CHLORIDES OF TUNGSTEN.** When metallic tungsten is heated in chlorine, it burns and forms a red crystalline compound, which is fusible and volatile, and which, according to Wöhler, becomes blue in water,

forming muriatic acid and depositing a suboxide. It is soluble in caustic potassa with the evolution of hydrogen, and yields tungstate of potassa and chloride of potassium. A similar compound appears to be formed when sulphuret of tungsten is heated in chlorine, which condenses in long acicular crystals, and is resolved into a red vapour when heated. These chlorides appear to consist of

Tungsten . . . . .	1	..	100	..	58
Chlorine . . . . .	2	..	72	..	42
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		172		100

When oxide of tungsten is heated in a current of chlorine, it burns, and forms a *perchloride*, which condenses in yellowish-white plates; it is extremely volatile, and when exposed to air or moisture forms muriatic and tungstic acids; hence it is inferred to consist of

Tungsten . . . . .	1	..	100	..	48.1
Chlorine . . . . .	3	..	108	..	51.9
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		208		100.0

**SULPHURETS OF TUNGSTEN.** When 1 part of tungstic acid is mixed with 6 of cinnabar, and heated intensely for half an hour; or when the vapour of sulphur, or sulphuretted hydrogen is passed over tungstic acid heated intensely in a porcelain tube, a black powder is obtained, which assumes metallic lustre by friction, and which consists, according to Berzelius, of 100 tungsten + 33.6 sulphur: it is therefore a *bisulphuret*; ( $tu + 2S$ ).

When tungstic acid is dissolved in hydrosulphuret of ammonia, or of potassium, and precipitated by an acid, a compound falls of a dirty-yellow colour, and somewhat soluble in water; it becomes darker coloured when dried, and when heated in close vessels, first gives off a little water, and then its excess of sulphur; it leaves the bisulphuret. This appears to be a *tersulphuret*: ( $tu + 3S$ ).

**PHOSPHURET OF TUNGSTEN** may be formed, but has not been examined. (Berzelius.)

*Before the blowpipe* TUNGSTIC ACID becomes upon charcoal at first brownish-yellow, is then reduced to a brown oxide, and lastly, becomes black without melting or smoking. With microcosmic salt it forms in the interior flame a pure blue glass, without any violet tinge; in the exterior flame this colour disappears, and appears again in the interior. With borax, in the internal flame, and in small proportion, it forms a colourless glass, which, by increasing the proportion of acid, becomes dirty-gray, and then reddish. By long exposure to the external flame it is rendered transparent, but as it cools it becomes muddy, whitish, and changeable into red when seen by daylight. It is not reduced.

### § XXVIII. COLUMBIUM.

THIS metal was discovered in 1801 by Mr. Hatchett, in a mineral from North America. It was afterwards found combined with the oxides of iron and manganese, and also with yttria, in the Swedish minerals called *tantalite* and *ytthro-tantalite*. Tantalite is chiefly found in octoëdral

crystals, and in masses of a black or gray colour, in Finland. Its specific gravity is 7.9, and it contains, according to Ekeberg, 80 oxide of columbium, 12 oxide of iron, and 8 oxide of manganese. Ytthro-tantalite is found at Ytterby, in Sweden. It contains about 45 *per cent.* of oxide of columbium. Its colour is dark gray, its lustre shining, and somewhat metallic.

Columbium was discovered in these minerals by M. Ekeberg, and, considering it as a *new* metal, he called it *tantalum*. In 1809 (*Phil. Trans.*) Dr. Wollaston re-examined these, and the specimen in the British Museum originally analysed by Mr. Hatchett, and demonstrated the identity of columbium and tantalum. As the former name was given to this body by its original discoverer, it is here retained.

Columbite or tantalite may be decomposed by the following process:—Mix 5 parts of the finely-powdered mineral with 25 of carbonate of potassa, and 10 of borax; fuse the mixture, and when cold, digest it in muriatic acid; this dissolves every thing except the peroxide of columbium, which remains in the form of a white powder. (Wollaston, *Phil. Trans.*, 1809, p. 248.) From 5 grains of columbite, Dr. Wollaston obtained 4. grains of oxide of columbium, 0.75 of oxide of iron, and 0.25 of oxide of manganese; and from 5 grains of tantalite he procured 4.25 of oxide of columbium, 0.50 of oxide of iron, and 0.2 of oxide of manganese.

Berzelius obtained metallic columbium by heating potassium with the *potasso-fluoride of columbium*, and washing the reduced mass with water. It remains in the form of a black powder: by pressure it acquires lustre and the colour of iron; it burns at a red-heat into a whitish oxide. Its specific gravity is about 6. It is insoluble, or nearly so, in muriatic, nitric, and nitro-muriatic acids. Heated to redness, it burns into columbic acid. Mixed with nitre, and projected into a red-hot crucible, it detonates, and is oxidized. It forms alloys with other metals. (*Ann. de Chim. et Phys.*, iii., 140.) Its equivalent may be assumed as 185. (184 Gmelin, 185 Turner.)

OXIDE OF COLUMBIUM. When columbic acid is intensely heated for an hour and a half in a charcoal crucible, it is superficially reduced to a metallic state, but the interior portion is a dark-gray, and brown when pulverised; it is insoluble in the acids, but may be peroxidized by fusion with potassa: it burns when heated in the air. It exists *native* in the tantalite of Kimito, in Finland, combined with protoxides of iron and manganese. This mineral has a specific gravity = 7.9, and becomes of a cinnamon-brown colour when finely powdered. Oxide of columbium consists of

							Berzelius.
Columbium . . . . .	1	..	185	..	92.04	..	92.02
Oxygen . . . . .	2	..	16	..	7.96	..	7.98
	1		201		100.00		100.00

COLUMBIC ACID. ( $col + 3O$ ) or  $col'$ . The best process for obtaining columbic acid consists in fusing the ore of columbium with bisulphate of potassa, and proceeding as directed by Berzelius. (*Lehrbuch*). An easier, but less economical process, is that of Ekeberg, in which the ore

is finely powdered, and fused with caustic potassa; a soluble columbate of potassa is formed, from which the columbic acid may be precipitated, as a white *hydrate*, by the acids. Dr. Wollaston's process above given may also be used. The characters of columbic acid are very well marked. In its anhydrous state, after having been ignited, it is nearly insoluble in muriatic, nitric, and sulphuric acids; it is soluble in potassa, and carbonate of potassa; 8 grains of the latter, fused with 1 of the oxide, render it soluble in water. It is much less soluble in soda, and only retained while hot.

The hydrated columbic acid dissolves in nitric, muriatic, and sulphuric acids, and, according to Dr. Wollaston, in tartaric, citric, and oxalic acids. In this state, and whilst moist, it is abundantly soluble in solution of binoxalate of potassa, but scarcely at all in bitartrate of potassa. The oxalic solution is colourless; alkalis throw down the columbic acid; ferrocyanuret of potassium produces in it a yellow precipitate; infusion of galls gives it an orange colour, and when added in excess produces a precipitate; the hydrosulphurets occasion a white precipitate, with the evolution of sulphuretted hydrogen. Columbic acid consists of

		Berzelius					
Columbium	. . . . . 1	. .	185	. .	88.5	. .	88.49
Oxygen	. . . . . 3	. .	24	. .	11.5	. .	11.51
	1		209		100.0		100.00

COLUMBATE OF AMMONIA is produced by digesting hydrated-columbic acid in ammonia: it is insoluble, and at a red-heat yields ammonia and water: the ammonia escapes by long exposure to air. Carbonate of ammonia only takes up a trace of columbic acid.

COLUMBATE OF POTASSA is obtained by fusing columbic acid with carbonate of potassa, pulverising the product, and digesting it in water. The columbate of potassa, being nearly insoluble in a solution of carbonate of potassa, remains, and after it has been washed with a little cold water, it may be dissolved in boiling water; when this solution is distilled to dryness, a saline uncrystallizable mass remains, of an unpleasant metallic taste: its solution is precipitated by all the acids, not excepting the carbonic.

COLUMBATE OF SODA may be obtained as the preceding: it is less soluble, and is almost entirely deposited, as a white powder, during the cooling of its boiling aqueous solution.

COLUMBATE OF LIME and of BARYTA are insoluble white powders.

FERRO-COLUMBATE OF MANGANESE has been adverted to above as a natural product, under the name of *columbite* or *tantalite*.

The remaining binary salts of the columbic acid with the oxides have not been examined.

CHLORIDE OF COLUMBIUM. The metal burns when heated in chlorine, producing a yellow vapour like chlorine, which condenses into a white pulverulent substance, which on contact of water is converted, with rapid action and increase of temperature, into muriatic and columbic acids: this is therefore a *terchloride*. ( $col + 3c.$ )

FLUORIDE OF COLUMBIUM. When hydrated columbic acid is dissolved

in hydrofluoric acid, and evaporated at a temperature of about  $86^{\circ}$ , crystals are obtained, which dissolve without residue in water, and which consist of fluoride of columbium and hydrofluoric acid. (Berzelius.) This compound combines with other fluorides to form *columbo-fluorides*.

**SULPHURET OF COLUMBIUM.** When columbium is heated in the vapour of sulphur it burns into a sulphuret: a similar compound is formed by passing the vapour of sulphuret of carbon over columbic acid heated to whiteness in a porcelain tube. In the air this sulphuret burns into columbic acid, which obstinately retains a portion of sulphuric acid. Berzelius considers this as a *tersulphuret*, ( $COl + 3S$ ).

The remaining combinations of columbium have not been sufficiently examined to require notice: the characters of its compounds will be evident from the preceding paragraphs.

## § XXIX. MERCURY.

THE principal ore of this metal is the *sulphuret*, or *native cinnabar*, from which the mercury is separated by distillation with quicklime or iron-filings.

Mercury ( $\S$ ) is a brilliant white metal, having much of the colour of silver, whence the terms *hydrargyrum*, *argentum vivum*, and *quicksilver*. It has been known from very remote ages. It is liquid at all common temperatures; solid and malleable at  $-40^{\circ}$ , and contracts considerably at the moment of congelation; its specific gravity in the frozen state being 15.6. It boils and becomes vapour at about  $670^{\circ}$ . Its specific gravity at  $60^{\circ}$  is 13.5; and the specific gravity of mercurial vapour is 6.97. (Dumas, *Ann de Chim. et Phys.*, xxxiii.) It is said to be sometimes adulterated with lead and bismuth, a fraud easily detected by the want of its due fluidity, and by its not being perfectly volatile, but leaving a residuum when boiled in a platinum or iron spoon. The best method of purifying mercury is to redistil it in an iron retort. The equivalent of mercury is 200, (202, Turner; 101, Gmelin; 100, Thomson,) at least this number is most consistent with the binary compounds of the metal, and with the constitution of the salts of its oxides. Gmelin, in adopting the number 101, regards the protoxide and protochloride as a dioxide and dichloride; that is, ( $2hg + o$ ) and ( $2hg + c$ .) Dr. Thomson also considers these compounds as a suboxide and subchloride. There are two circumstances which justify this atomic weight; one is, that the constant quantity obtained by multiplying the specific heat of mercury by its atomic number (see p. 149) requires that 100, or thereabouts, should be the equivalent; and the other, that the specific gravity of the vapour of mercury, in reference to hydrogen, is as 100 or 101 to 1.

*Native Mercury* occurs in small fluid globules, in most of the mines producing the ores of this metal.

• **MERCURY AND OXYGEN.** There are two oxides of mercury.

**PROTOXIDE OF MERCURY.** ( $hg + o$ .) This oxide is formed, when the protochloride of mercury is decomposed by triturating it in excess of solution of potassa, washing the product with cold water, and drying it at common temperature in a dark place, (Donovan, *Ann. of Phil.*, xiv.)

If heated, or exposed to the sun's rays, it is resolved into peroxide and metallic mercury. A preparation, often considered as nearly corresponding with this oxide, is directed in the *London Pharmacopœia*, under the name of *Hydrargyri oxidum cinereum*. It is made by boiling calomel with lime-water; but it is by no means a pure protoxide of mercury, and is so uncertain in its composition, as to be quite unfit for medical use. It is also supposed that the protoxide of mercury is contained in the *Pilula hydrargyri*, or *blue pill*, and in the *unguentum hydrargyri*, or *mercurial ointment*. Some have regarded these preparations as merely containing *finely-divided* mercury, and deny the possibility of oxydizing the metal, when pure, by mere agitation in the contact of atmospherical air, or trituration with viscid and oleaginous substances; it is certain that perfectly pure mercury, if at all thus acted on, is converted into an oxide extremely slowly, whilst mercury containing a little lead or bismuth, is speedily converted into a black powder. Some of the protosalts of mercury, especially the protonitrate, when carefully prepared, and decomposed by excess of caustic potassa, furnish a precipitate of protoxide of mercury; it requires to be washed with repeated affusions of cold water and carefully dried, first on bibulous paper, and then in a vacuum over sulphuric acid. Protoxide of mercury consists of

					Guibourt.	Donovan.	Foucrocy	Seftstrom.					
Mercury	1	..	200	..	96.1	..	95.69	..	96.04	..	96.16	..	96.2
Oxygen	1	..	8	..	3.9	..	4.31	..	3.96	..	3.84	..	3.8
	<u>1</u>		<u>208</u>		<u>100.0</u>		<u>100.00</u>		<u>100.00</u>		<u>100.00</u>		<u>100.0</u>

PEROXIDE OF MERCURY. ( $hg + 2 O.$ ) This oxide is produced by exposing mercury, heated nearly to its boiling-point, to the action of air. It becomes coated with reddish-brown scales, spangles, and crystals, and is ultimately entirely converted into a red crystallized mass, called in old pharmaceutical works, *precipitatum per se*, or *calcined mercury*. It is the *hydrargyri oxydum rubrum* of the *London Pharmacopœia*. It is most easily obtained by introducing into a flat-bottomed matrass, of the annexed shape (fig. 233) about four ounces of mercury, and placing it in a sand-bath, heated nearly to the boiling-point of the metal. In about a month's time nearly the whole is converted into oxide. Air is freely admitted by the tube, while its length prevents the escape of mercurial vapour, which condenses and falls back into the body of the vessel; the remaining portion of running mercury may be driven off by exposing it in a basin to a heat below redness.

This oxide may also be obtained by evaporating nitrate of mercury to dryness, and carefully exposing the residue to heat; or by precipitating the pernitrate of mercury by potassa, which produces a *hydrated peroxide of mercury*, and which, after thorough edulcoration, must be dried at a high heat. The purest peroxide, however, is that obtained by the first process. This oxide has an acrid metallic taste, and is poisonous. According to Thomson, Guibourt, and Donovan, it is very sparingly soluble in water, and the solution has a metallic taste, and is rendered brown by sulphuretted hydrogen; other chemists deny the solubility of the perfectly pure per-



oxide, and ascribe it to the presence of a trace of the pernitrate. When this oxide is heated, it acquires a black colour, but becomes again red on cooling; at a red-heat it evolves oxygen, and is reduced to the metallic state. When long exposed to light it becomes black upon the surface, in consequence, apparently, of superficial reduction to the state of protoxide. It should be entirely volatilized when placed upon a red-hot iron, for it is sometimes adulterated with red lead. Peroxide of mercury consists of

		Zaboada.	Rose.	Proust.	Donovan.	Fourcroy.	Seftstrom.
Mercury	1 . 200 .	92.12 .	90 .	91 .	92 .	92.75 .	92.68
Oxygen	2 . 16 .	7.88 .	10 .	9 .	8 .	7.25 .	7.32
	<u>1</u>	<u>216</u>	<u>100.00</u>	<u>100</u>	<u>100</u>	<u>100.00</u>	<u>100.00</u>

Both the oxides of mercury combine with the greater number of the acids, forming two distinct classes of salts, several of which are resolvable into salts with excess of base, and salts with excess of acid, so that the history of the saline combinations of mercury is thus rendered somewhat complex.

**HYDRARGYRATE OF AMMONIA: AMMONIURET OF MERCURY.** When peroxide of mercury is digested in liquid ammonia, a pale-yellow compound of the peroxide with 13.6 *per cent.* of ammonia is obtained. (Guibourt.) It is a compound of 3 atoms of peroxide, 2 of ammonia, and 4 of water. (Kane.)

**MERCURY AND CHLORINE** combine in two proportions, and form a protochloride and perchloride of mercury, corresponding in composition with the protoxide and peroxide. These compounds are often called *calomel* and *corrosive sublimate*.

**PROTOCHLORIDE OF MERCURY; CALOMEL. ( $hg + c.$ )** This compound is first mentioned by Crollius, early in the seventeenth century. The first directions for its preparation are given by Beguin, in the *Tyrocinium Chemicum*, published in 1608. He calls it *draco mitigatus*. Several other fanciful names have been applied to it, such as *aquila mitigata*, *manna metallorum*, *panchymagogum minerale*, *sublimatum dulce*, *mercurius dulcis*, &c.

The most usual mode of preparing calomel consists in triturating 4 parts of corrosive sublimate with 3 of mercury, until the globules disappear, and the whole assumes the appearance of an homogeneous gray powder, which is introduced into a matrass, placed in a sand-heat, and gradually raised to redness. The protochloride sublimes, mixed with a little of the perchloride, the greater part of which, however, being more volatile than the calomel, rises higher in the matrass; that which adheres to the protochloride may be separated, by reducing the whole to a fine powder, and washing in large quantities of hot distilled water. Pure protochloride of mercury, in the form of a yellowish-white insipid powder, remains.

It was formerly the custom to submit this product to very numerous sublimations, under the idea of rendering it *mild*; but these often tended to the production of corrosive sublimate; and the calomel of the first sublimation, especially if a little excess of mercury be found in it, is often more pure than that afforded by subsequent operations.



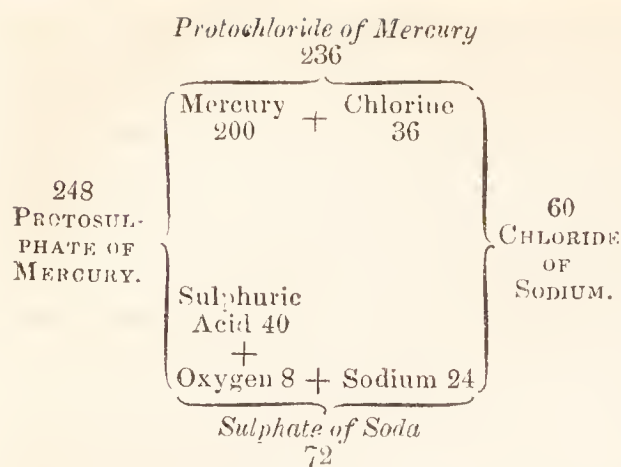
In this process the operation consists in reducing the perchloride to the state of protochloride by the addition of mercury. Various modes have, however, been adopted for the direct formation of the protochloride: two of these may here be noticed, of which the first is in the *humid way*, as devised by Scheele and Chenevix. It is as follows: Form a protonitrate of mercury by dissolving as much mercury as possible in nitric acid; then dissolve in boiling water a quantity of common salt, equal to half the weight of the mercury used, and render the solution sensibly sour by muriatic acid, and pour the hot nitrate of mercury into it. Wash and dry the precipitate. If this process be carefully performed, and the precipitate thoroughlyedulcorated, the calomel is said to be sufficiently pure; but I should not recommend it for pharmaceutical use.

The second process, however, or that by which calomel is directly formed in the *dry way*, appears, on the whole, the least exceptionable for the production of this very important article of pharmacy. It is as follows: Boil 2 pounds of mercury with 30 ounces of sulphuric acid in a glass vessel, until the sulphate of mercury is dry. When it has cooled, rub it with two pounds of mercury in an earthenware mortar, till they are well mixed. Then add a pound and a half of chloride of sodium, and rub them together until globules are no longer visible. Put this mixture into a proper vessel, and heat it gradually to redness; the protochloride of mercury, or calomel, sublimes, and condenses in various forms, according to the rapidity of the operation and the form and capacity of the subliming vessel. If intended for medicinal use, it should be cautiously reduced to an impalpable powder, and washed with repeated affusions of hot distilled water, till it becomes perfectly tasteless, and till the water which runs off is not discoloured by the addition of an aqueous solution of sulphuretted hydrogen.

This process has many advantages over the more usual method. The sulphate of mercury may be formed by boiling the metal with sulphuric acid to dryness in a cast-iron vessel, which should be conveniently arranged for the escape of the abundant fumes of sulphurous acid developed by the action of the mercury, and which are often a serious nuisance to the neighbourhood. They may be very effectually annihilated by suffering them to pass through a long flue and lofty chimney, mixed with abundance of coal smoke. The *persulphate* of mercury is triturated with a sufficient quantity of metallic mercury to convert it into a *protosulphate*, and then mixed with a due proportion of common salt, and subjected to sublimation. Protosulphate of mercury is a compound of

1 proportional of protoxide of mercury	.	.	.	.	= 208
1 „ „ sulphuric acid	.	.	.	.	= 40
					248

To convert it into protochloride of mercury, it is mixed with one proportional of chloride of sodium, the chlorine of which combines with the mercury of the oxide of mercury in the protosulphate, to form a protochloride, whilst its sodium becomes sulphate of soda, as shown in the following diagram, in which the ORIGINAL COMPOUNDS are printed in small capitals, the *products* in italics, and the component substances in common type: the equivalent numbers are affixed to the respective agents.



In washing calomel, muriate of ammonia is often used, in consequence of the extreme solubility which it confers on the perchloride of mercury: common salt answers equally well, and is cheaper; but it deserves notice in relation to this part of the process, that calomel *boiled* with solution of sal-ammoniac, or of common salt, is resolved into metal-

lic mercury and corrosive sublimate; the washings, therefore, where these salts are employed, should be with their cold solutions; but, in general, it is perhaps safer to wash with hot distilled water only, which, when conjoined with perfect levigation, and tested as above directed, is very effective.

The form in which calomel sublimes depends much upon the dimensions and temperature of the subliming vessels. In small vessels it generally condenses in a crystalline cake, the interior surface of which is often covered with beautiful quadrangular prismatic crystals (Brooke, *Ann. of Phil.*, ii., 427, 2nd series), transparent, and of a texture somewhat elastic or horny: in this state it acquires, by the necessary rubbing into powder, a decidedly yellow or buff colour, more or less deep according to the degree of trituration which it has undergone. If, on the contrary, the calomel be sublimed into a very capacious and cold receiver, it falls in a most impalpable and perfectly white powder, which only requires due elutriation to fit it for use; it then remains perfectly colourless. By a modification of the process, it may be suffered as it sublimes to fall into water, according to Mr. Jewell's patent.

The above circumstances, too, account for the various appearances under which calomel occasionally presents itself in commerce: it may be added, that the buff aspect of this substance indicates the absence of corrosive sublimate; though it by no means follows as a consequence, that when snow-white it contains it. When the surface of massive sublimed calomel is scratched, it always exhibits a buff-colour: it also becomes yellow when heated, but loses this tint as it again cools.

Calomel should be perfectly tasteless, inodorous, and insoluble in water. Its specific gravity is 7.2. At a heat somewhat below redness it rises in vapour, without previous fusion; but it fuses when subjected to heat under pressure. The density of its vapour is 8.2; or 119 in reference to hydrogen as unity. When scratched or broken in the dark, it phosphoresces. It consists of

Mercury . . . .	1	..	200	..	84.74	.. Turner. Davy. Zaboda.
Chlorine . . . .	1	..	36	..	15.36	.. 85 15
	1		236		100.00	100.

It is decomposed by the fixed alkalis and by ammonia, and protoxide of mercury is one of the results.

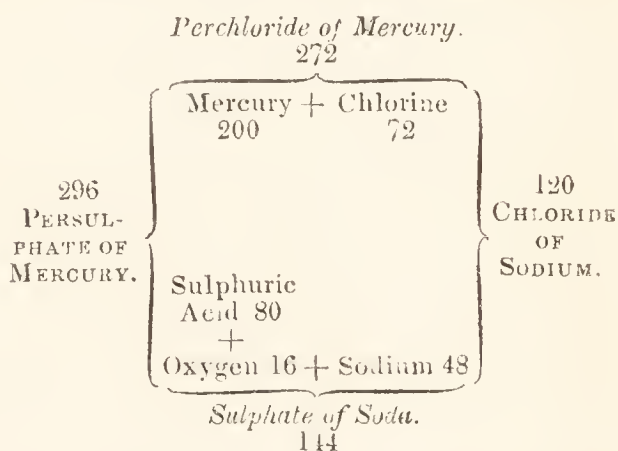
*Native Protochloride of Mercury*, or *Mercurial Horn Ore*, has been found in Germany, France, and Spain, usually crystallized, and sometimes incrusting and massive: it is rare.

PERCHLORIDE OF MERCURY; BICHLORIDE OF MERCURY; OXYMURIATE OF MERCURY; CORROSIVE SUBLIMATE. ( $hg + 2c.$ ) When mercury is heated in excess of chlorine, it burns with a pale flame, the gas is absorbed, and a white volatile substance rises, which is the *perchloride*. It may also be obtained by dissolving peroxide of mercury in muriatic acid, evaporating to dryness, redissolving in water, and crystallizing.

The ordinary process for making corrosive sublimate consists in exposing a mixture of chloride of sodium and persulphate of mercury, to heat in a proper subliming-vessel.

The persulphate is formed by boiling 2 lbs. of mercury with 30 oz. of sulphuric acid to dryness; it is then rubbed to powder with 4 lbs. of chloride of sodium, and the mixture put into a large flask or into an earthen subliming-pan, and exposed to a heat gradually raised to redness.

In this process the original substances are decomposed, *perchloride of mercury* sublimes, and *sulphate of soda* is the residue. The object, then, of the operation is, to obtain a compound of *one* proportional of mercury and *two* of chlorine, which is effected by the mutual decomposition of *one* proportional of persulphate of mercury, = 296, and *two* proportionals of chloride of sodium,  $60 \times 2 = 120$ , as shown in the annexed diagram:—



The *persulphate of mercury* is generally prepared upon the large scale, by heating the acid and metal in an iron pot, proper means being adopted to carry off the copious fumes of sulphurous acid arising from the decomposition of a portion of the sulphuric acid, during the peroxidizement of the mercury. The whole is then evaporated to dryness, and the subsequent sublimation is performed in glass, earthenware, or iron vessels, their form and arrangement being much dependent upon the quantity of materials employed.

Perchloride of mercury has an acrid nauseous taste, leaving a permanent metallic and astringent flavour upon the tongue. Its specific gravity is 5.2. It is usually met with in the shops in the form of white semi-transparent and imperfectly crystallized masses, or in powder. It frequently exhibits prismatic crystals upon the inner surfaces of the sublimed cakes (Brooke, *Ann. of Phil.*, 2nd ser., vi., 285). It is soluble in 20 parts of water, at the temperature of 60°, and boiling water takes up nearly half its weight, and as the solution cools it deposits quadrangular prismatic crystals: it is more copiously soluble in alcohol and in ether, and when ether is agitated with the aqueous solution it abstracts the perchloride from the water. When heated, it readily fuses, boils, and entirely sublimes in the form of a dense white vapour, powerfully affecting the nose and mouth. It dissolves without decomposition in muriatic acid, but is insoluble in concentrated nitric and sulphuric acids. Muriatic acid of the specific gravity 1.158, at the temperature of 60°, dissolves about its own weight, and the solution, when cooled to about 40°, concretes into a mass of acicular crystals.

When solution of *perchloride of mercury* is decomposed by potassa, soda, or lime, a yellow precipitate is thrown down, which is a hydrated *peroxide of mercury*. Such a mixture of a pint of lime-water with a drachm of corrosive sublimate was formerly much used as an application to venereal ulcers, under the name of *aqua phagedænica*, or *red lotion*. It is in fact a solution containing undecomposed corrosive sublimate and chloride of calcium (muriate of lime) mixed with peroxide of mercury, *two* proportionals of lime being required for the decomposition of *one* proportional of corrosive sublimate, as shown in the annexed diagram, which also exhibits the theory of the decomposition.

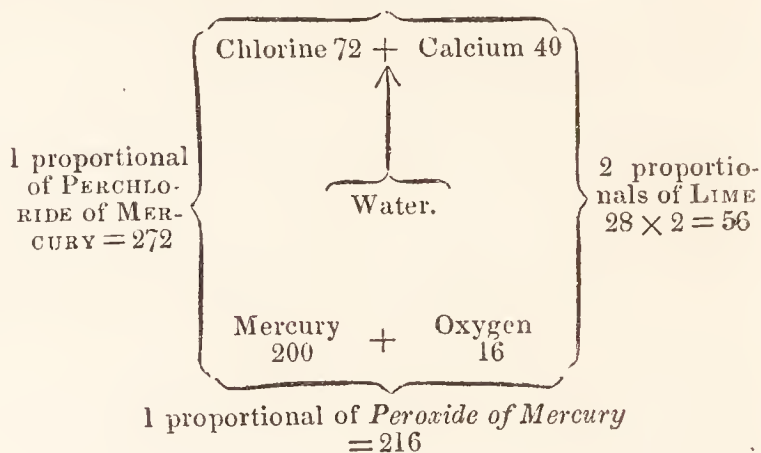
When *protochloride of mercury* or calomel is similarly decomposed, a portion of *protoxide of mercury* is the result, as in the annexed diagram, and the mixture which is known in pharmacy under the name of *black lotion*, is obtained.

Perchloride of mercury consists of

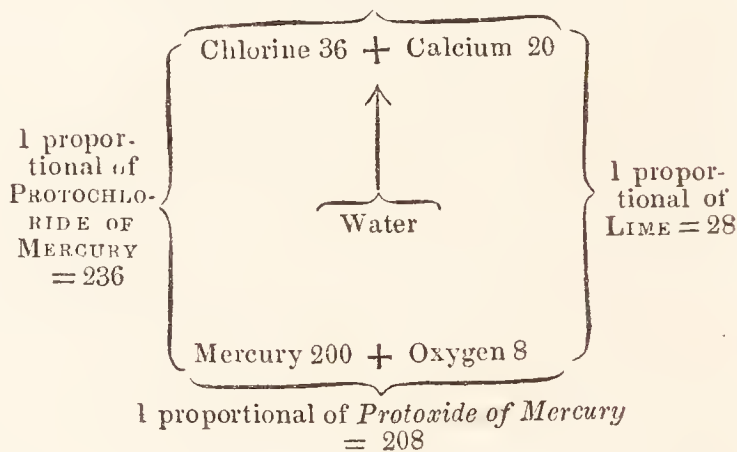
Mercury . . . .	1		200		73.53
Chlorine . . . .	2		72		26.47
	1		272		100.00

**HYDRARGO-PERCHLORIDES.** It has long been known that muriate of ammonia considerably increases the solubility of corrosive sublimate, one part rendering five parts soluble in rather less than five of water. This solution yields on evaporation the *sal alembroth* of the old chemists. Analogous combinations may also be obtained with other chlorides; thus, a solution composed of 7 parts of chloride of sodium and 20 of water dissolves 32 parts of corrosive sublimate, and deposits rhomboidal crystals, (J. Davy, *Phil. Trans.*, 1822, p. 364). In these compounds, the electro-positive chlorides, those of the alkaline bases, &c., act the part of *base* to the corrosive sublimate, and a class of salts which have been termed *hydrargo-perchlorides* is the result. These compounds have been examined in detail by Bonsdorff. (*Ann. de Chim. et Phys.*, xlv.) They generally contain 2 atoms of corrosive sublimate to 1 of the basic chloride. Some of them, such as those of calcium, lithium, magnesium, and zinc, are deliquescent; those of iron and of manganese are isomorphous, and

2 proportionals of *Chloride of Calcium*.  
56 × 2 = 112



1 proportional of *Chloride of Calcium*  
= 56



crystallize in the form of rhombic prisms. Mr. Donovan has shown that a solution of corrosive sublimate dissolves and combines with peroxide of mercury, forming a compound very sparingly soluble in water, and which separates from it in granular brown crystals.

There is a compound in which perchloride of mercury appears to act the part of acid, to a base composed of ammonia and peroxide of mercury. This combination is thrown down in the form of a white powder, when ammonia is poured into a solution of corrosive sublimate; or when a mixed solution of corrosive sublimate and muriate of ammonia is decomposed by solution of potassa. It is the *white precipitate of mercury* of Pharmacy, and contains, according to Hennel, elements equivalent to 1 atom of peroxide of mercury, and 1 of muriate of ammonia. (*Quar. Jour.*, xviii., 297.) From the elaborate examination of some of these compounds by Professor Kane, of Dublin, (*Trans. Royal Irish Academy*, xvii.,) it would appear most probable that *white precipitate* is constituted of

Bichloride of mercury	. . . . . 2	. . . . . 544	. . . . . 68.5
Ammonia	. . . . . 2	. . . . . 34	. . . . . 4.2
Peroxide of mercury	. . . . . 1	. . . . . 216	. . . . . 27.3
	1	794	100.0

According to Mr. Kane, the gray compound obtained by the action of ammonia on calomel, is analogous to the above, the mercury being in protocombination: it appears to consist of 1 atom of protochloride of mercury, 1 atom of ammonia, and 1 atom of protoxide of mercury.

CHLORATE OF MERCURY. Chloric acid dissolves both the oxides of mercury; the *protochlorate* has the appearance of a yellowish granular powder, sparingly soluble in hot water, and of a mercurial taste. The *perchlorate* forms white acicular crystals, having the acrid flavour of the perchloride, and soluble in 4 parts of water at 60°. (*Vauquelin, Ann. de Chim.*, xcv.)

MERCURY AND IODINE; PROTIODIDE OF MERCURY. (*hg + i*) This compound is most readily obtained by adding a solution of iodide of potassium to one of protonitrate of mercury; it falls in the form of a dirty yellow powder. When rapidly heated in a glass tube, it fuses, and sublimes unaltered. When gently heated, or when long exposed to light, it is resolved into mercury and periodide. It consists of

Mercury	. . . . . 1	. . . . . 200	. . . . . 61.5
Iodine	. . . . . 1	. . . . . 125	. . . . . 38.5
	1	325	100.0

PERIODIDE OF MERCURY (*hg + 2i*) is of a bright scarlet, and is precipitated by the addition of a solution of iodide of potassium to one of corrosive sublimate or of pernitrates of mercury; it is easily fusible, and assumes a yellow colour: it sublimes in rhomboidal scales, at first yellow, but becoming red on cooling. Acids and alcohol dissolve it by the aid of heat, and as the solutions cool it separates in more or less perfect crystals; it dissolves also in solutions of the mercurial salts and of iodide of potassium. It is precipitated by sulphuric acid from its solution in caustic potassa. It consists of

Mercury . . . .	1	..	200	..	44.5
Iodine . . . .	2	..	250	..	55.5
	1		450		100.0

The periodide, like the perchloride of mercury, forms salts with the iodides of the electropositive bases, which may be termed *hydrargo-iodides*. These compounds of potassium, sodium, iron, and zinc, have been examined by Bonsdorff. (*Ann. de Chim. et Phys.*, xliv.)

**IODATE OF MERCURY.** Iodate of potassa occasions a white insoluble precipitate in protonitrate of mercury, but not in the pernitrate; hence the periodate appears to be a soluble salt.

**BROMIDES OF MERCURY.** Bromide of potassium occasions a white curdy precipitate in the protonitrate of mercury, which is a *protobromide of mercury*: the *perbromide* may be obtained by digesting the protobromide with bromine, or by the action of bromine on peroxide of mercury; it is a white crystallizable compound, fusible, volatile, and soluble in water and in alcohol. It forms double salts (*hydrargo-bromides*) with the bromides of the alkaline bases.

The *Bromates of Mercury* have not been examined.

**FLUORIDES OF MERCURY.** Hydrofluoric acid occasions no precipitate in the protonitrate of mercury, and when the mixture is evaporated, the acid escapes, and leaves the mercurial salt unchanged. When hydrofluoric acid is poured upon peroxide of mercury, it acquires an orange-colour, and is dissolved upon the addition of water. The solution furnishes yellow prismatic crystals, which, by the action of hot water, are resolved into a soluble and insoluble compound.

**MERCURY AND NITRIC ACID.** Nitric acid is rapidly decomposed by mercury; nitrous acid, and nitric oxide gases are evolved, and either a *protonitrate* or a *pernitrate* of mercury are obtained, according to the mode in which the solution is performed.

**PROTONITRATE OF MERCURY** ( $hg + o + n'$ ) is best obtained by dissolving the metal in a cold and dilute acid, consisting of one part of acid and three of water; the metal should be added in small successive portions until the acid ceases to act upon it, and care should be taken to keep the whole cold. This solution deposits transparent crystals, which appear to be modified octoëdra, and which consist of the protoxide of mercury combined with nitric acid. They are soluble without decomposition in cold water, and the solution affords black precipitates, upon the addition of excess of the alkalis. Small quantities of the caustic alkalis dropped into this solution, occasion yellowish and gray precipitates, which appear to be mixtures of the oxide and subnitrate. The *crystallized protonitrate* contains, according to Mitscherlich, 2 atoms of water. The theoretic composition of the *anhydrous protonitrate* is

Protoxide of mercury .	1	..	208	..	79.5
Nitric acid . . . .	1	..	54	..	20.5
	1		262		100.0

As a test, a solution of protonitrate of mercury is useful in the following cases; with sulphuretted hydrogen it yields a *black* precipitate, with hydriodic salts *greenish-yellow*, with muriatic acid and salts *white*, with ammonia *black*, with fixed alkalis *gray*, with chromic acid *red*, with arse-

nious acid *white* or *straw-colour*: it discolours an extremely dilute solution of gold, rendering it *dark-brown*, and of platinum *yellowish-brown*, or if very dilute, *yellow*. It throws down white flakes from albuminous solutions.

**PERNITRATE OF MERCURY.** When mercury is dissolved in hot and concentrated nitric acid, nitric oxide is evolved, the metal becomes peroxidized, and furnishes prismatic crystals of the pernitrate. They are soluble, without decomposition, in cold water, and their solution furnishes a yellow precipitate of hydrated peroxide of mercury, upon the addition of potassa or soda; ammonia forms a white precipitate, which is a *triple nitrate of mercury and ammonia*. The *theoretic* composition of the neutral pernitrate of mercury is

Peroxide of Mercury	.	1	..	216	..	66.5
Nitric acid	.	2	..	108	..	33.5
		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
		1		324		100.0

But according to Thomson, the above crystals consist of *one* proportional of the peroxide, and *one* of nitric acid ( $hg + 2O + n'$ ); Mitscherlich also states that the true *neutral* salt cannot exist in a solid form.

When the precautions in forming the nitrates above described are not attended to, the solution usually contains a mixture of the two nitrates, and furnishes a precipitate with the alkalis, composed of both oxides. The pernitrate is most certainly formed by dissolving the red oxide in nitric acid.

The pernitrate of mercury acts as a test, like corrosive sublimate, but it precipitates tincture of galls, of an orange-colour, which is not the case with sublimate.

**SUBNITRATES OF MERCURY.** When hot water is poured upon *pernitrate of mercury*, a yellow insoluble powder separates from it, which is a *subpernitrate*, the *nitrous turpeth* of old writers; and a *superpernitrate* remains in solution. It seems probable that the *protonitrate* is also capable of affording a sub and a super salt, but these compounds have hitherto been but imperfectly investigated, and new researches are wanting to establish their nature and composition. Grouvelle (*Ann. de Chim. et Phys.* xix.) found the yellow *subpernitrate* to consist of

Peroxide of mercury	.	2	..	432	..	89
Nitric acid	.	1	..	54	..	11
		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
		1		486		100

**NITRICO-OXIDE OF MERCURY.** When the nitrates of mercury are exposed to heat gradually raised to dull redness, nitric acid is given off; and a red substance remains, consisting of peroxide of mercury with a small portion of adhering nitrate. This is used in pharmacy as an escharotic, and is called in the *London Pharmacopœia*, *hydrargyri nitrico-oxidum*. It is difficult in this process so to apply the heat, as to expel the acid, without at the same time evolving oxygen from the remaining oxide and evaporating part of the mercury. We find, therefore, nitric acid generally remaining in the compound. The nitrate requires to be constantly stirred during the process, which is usually performed in a cast-iron pot; the operator will find it advantageous to

prepare the solution and partly to evaporate it in a retort with an annexed receiver containing a little water, by which, if any quantity of materials is employed, he will save a part of the acid. The product, when well prepared, is of a brilliant red-colour, with a shade of orange; when not in very fine powder it has a glistening scaly appearance; at a red-heat it is decomposed and entirely dissipated, provided it be not adulterated, as it sometimes is, with red-lead: it has an acrid taste, is very sparingly soluble in water, and readily soluble without effervescence in nitric acid. The proportion of subpernitrate of mercury remaining in this preparation is variable; but some is always to be detected, for, when decomposed by heat, the evolved oxygen is found to be mixed with a portion of nitrogen: it therefore should never be used in medicine as a substitute for pure peroxide of mercury. When washed with and triturated in a dilute solution of potassa,edulcorated with distilled water, and carefully dried, it may be regarded as nearly pure peroxide of mercury. In this state it is called *arcanum corallinum* in some of the older Pharmacopœiæ.

MERCURY AND SULPHUR; PROTOSULPHURET OF MERCURY. ( $hg + S$ .) When one part of mercury is triturated for some time with three of sulphur, a black tasteless compound is obtained, which was called in old pharmacy *Ethiops Mineral*; it is the *hydrargyri sulphuretum nigrum* of the Pharmacopœia, and is often regarded as a definite sulphuret, but when boiled in solution of potassa, sulphur is taken up, and bisulphuret of mercury remains; so that it is probably a mixture of sulphur and of the bisulphuret. According to Taddei, an Ethiops mineral may be quickly formed by the following process. (*Gior. di Fisica*, iv., 12.) Put one part of sulphuret of potassa with three of mercury into a mortar, and triturate with a little water, until the whole forms a homogeneous black paste; then add flowers of sulphur equal in weight to the mercury, and mix the whole: wash with repeated affusions of water, till the alkaline sulphuret is removed, and carefully dry the remaining Ethiops.

When sulphuretted hydrogen is passed through a dilute solution of protonitrate of mercury, or through a mixture of very finely divided calomel and water, a black powder is thrown down, which is a true protosulphuret. When it is boiled with nitric acid, it is converted into a sulphate of mercury: heated to redness, metallic mercury escapes, and bisulphuret sublimes. It consists, according to Guibourt (*Ann. de Chim. et Phys.*, i.), of 100 mercury + 8.2 sulphur, numbers which correspond to

Mercury . . . .	1	. .	200	.	92.5
Sulphur . . . .	1	. .	16	.	7.5
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>		<hr style="width: 100%;"/>
	1		216		100.0

BISULPHURET OF MERCURY; VERMILION; CINNABAR. ( $hg + 2S$ .) In the manufacture of cinnabar, eight parts of mercury are mixed in an iron pot with one of sulphur, and made to combine by a moderate heat, and constant stirring: this compound is then transferred to a glass subliming-vessel (on a small scale, a Florence flask answers perfectly,) and heated to redness in a sand-bath; a quantity of mercury and of sulphur evaporate, and a sublimate forms, which is removed, and rubbed or levigated into a very fine powder. If mercury and sulphur be heated together in large quantities, the action is so intense at the moment of



their combination as to occasion a slight explosion and flame; sulphuretted hydrogen is also evolved.

Cinnabar is not altered by exposure to air or moisture; when heated to dull redness in an open vessel, the sulphur forms sulphurous acid, and the mercury escapes in vapour. It is decomposed by distillation with fixed alkalis, lime, and baryta, and by several of the metals. When adulterated with red-lead it is not entirely volatile. It is insoluble in nitric and muriatic acids, but nitromuriatic acid acts upon, and decomposes it even in the cold. Boiled in sulphuric acid, sulphurous acid is evolved, and a sulphate of mercury formed.

Cinnabar may be made in the humid way, by long trituration of mercury and sulphur in solution of potassa. (Nicholson's *Journal*, 4to., ii.) When a solution of corrosive sublimate is added to excess of hydrosulphuret of ammonia, a black precipitate falls, which acquires the colour of cinnabar when sublimed. This sulphuret consists of

					Seftstrom.	Guibourt.	Seguin.	Proust.
Mercury	. 1	.. 200	.. 86.2	.. 86.29	.. 86.21	.. 85.5	.. 85	
Sulphur.	. 2	.. 32	.. 13.8	.. 13.71	.. 13.79	.. 14.5	.. 15	
	<u>1</u>	<u>232</u>	<u>100.0</u>	<u>100.00</u>	<u>100.00</u>	<u>100.0</u>	<u>100</u>	

*Native Cinnabar* is the principal ore of mercury: it occurs massive and crystallized in six-sided prisms, rhombs, and octoëdra. It is of various colours, sometimes appearing steel-gray, at others bright-red. It occurs in Hungary, France, and Spain, in Europe; in Siberia, and Japan, in Asia; and in considerable quantities in South America. The mines of Almaden, and of New Spain, are the most productive, and furnish fine cabinet specimens. Native mercury, and native amalgam of silver sometimes accompany it.

**HYPOSULPHITES OF MERCURY.** When a solution of a hyposulphite is poured into a very dilute solution of protonitrate of mercury it occasions a black precipitate, which, however, is probably not a true hyposulphite. The nature of these compounds has not been satisfactorily ascertained.

**SULPHITES OF MERCURY and HYPOSULPHATES OF MERCURY** have not been examined.

**MERCURY AND SULPHURIC ACID; SULPHATES OF MERCURY; PROTOSULPHATE OF MERCURY.** ( $hg + o + s'$ .) When one part of mercury is digested in a moderate heat with one and a half of sulphuric acid, sulphurous acid gas is evolved, and a white deliquescent mass is obtained, which, washed with cold water, affords a very difficultly soluble white salt, which is a *protosulphate of mercury*. The same salt is thrown down, when sulphuric acid or sulphate of soda is added to a solution of protonitrate of mercury. It requires 500 parts of cold and 300 of boiling water for its solution, and crystallizes in prisms. According to Fourcroy, it is soluble in dilute sulphuric acid, and thus forms a crystallizable *supersulphate*. Its solution in boiling water is decomposed by the fixed alkalis, which first throw down a subsalt, and when added in excess separate the black protoxide. This salt, when anhydrous, consists of

Protoxide of mercury	. 1	. . 208	. . 83.8
Sulphuric acid	. . . . 1	. . 40	. . 16.2
	<u>1</u>	<u>248</u>	<u>100.0</u>

PERSULPHATE OF MERCURY. ( $hg + 2O + 2S'$ ). If five parts of sulphuric acid be boiled to dryness with four of mercury, a white crystalline mass of *persulphate of mercury* is obtained.

This salt cannot exist in solution in the neutral state, for water resolves it into a soluble *supersalt* and an insoluble *subsalt*. The soluble portion may be obtained by evaporation in the form of deliquescent acicular crystals. The subsalt, when triturated with boiling water, acquires a yellow colour, and was formerly called *turpeth mineral*, from a similarity in its medical effects to the roots of the *convolvulus turpethum*: it is dangerously cathartic and emetic. It is not absolutely insoluble in water, but requires 2000 parts of cold and 300 boiling water for the purpose. The anhydrous persulphate of mercury consists of

Peroxide of mercury . . . . .	1	. .	216	. .	73
Sulphuric acid . . . . .	2	. .	80	. .	27
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		296		100.

AMMONIO-PERSULPHATE OF MERCURY is obtained in the form of a white and very difficultly soluble powder, by adding excess of ammonia to the persulphate. The fixed alkalis throw down from the persulphate a yellow precipitate of hydrated peroxide of mercury.

PHOSPHURET OF MERCURY may be formed by heating phosphorus with oxide of mercury, or with the protosulphuret; or by passing the vapour of phosphorus over calomel; or phosphuretted hydrogen through a solution of protonitrate of mercury. It varies in appearance according to the method of its production: its colour is brown or black.

Neither the HYPOPHOSPHITE nor PHOSPHITE OF MERCURY have been examined.

PHOSPHATES OF MERCURY. When phosphate of soda is dropped into *protonitrate* of mercury, a white crystalline precipitate falls, which is *protophosphate of mercury*. It is insoluble in water and in excess of phosphoric acid, and when intensely heated is decomposed, and leaves phosphoric acid. *Perphosphate of mercury* is thrown down from the *pernitrate* by the addition of phosphate of soda: it resembles the *protophosphate* in appearance, but it dissolves in excess of phosphoric acid.

SELENIURET OF MERCURY is a tin-coloured substance, which sublimes in shining scales at a temperature below its point of fusion.

BISELENIURET OF MERCURY is obtained as a gray crystalline mass, by fusing the seleniuret with selenium.

CARBONATES OF MERCURY. When solution of carbonate of potassa is dropped into *protonitrate* of mercury, a yellow *protocarbonate of mercury* is thrown down. The *percarbonate of mercury* is of a reddish colour.

MERCURY AND CYANOGEN; BICYANURET OF MERCURY. ( $hg + 2cy$ .) By digesting finely-powdered peroxide of mercury in hydrocyanic acid and water, or by boiling one part of finely-powdered oxide with two of pure Prussian blue, in eight parts of water, a solution is obtained, which, if filtered while hot, deposits, on cooling, yellowish-white crystals in the form of quadrangular prisms, of a metallic taste and very poisonous. They are much more soluble in hot than in cold water, and very sparingly soluble in alcohol. When oxide of mercury is brought into the contact

of the vapour of hydrocyanic acid they act intensely upon each other, and water and cyanuret of mercury are immediately formed. The attraction of mercury for cyanogen is so strong, that peroxide of mercury decomposes nearly all the metallic cyanurets, not excepting that of potassium. The salts of palladium, however, decompose the cyanuret of mercury.

Cyanuret of mercury is decomposed by heat, as in the process for obtaining cyanogen (p. 499); and if distilled with muriatic acid, hydrocyanic acid and chloride of mercury are formed. It also is decomposed by hydriodic acid and by sulphuretted hydrogen, an iodide and a sulphuret of mercury, and hydrocyanic acid, being formed. Nitric acid dissolves it without decomposition. It is decomposed when heated with sulphuric acid. The alkalis do not act upon this cyanuret.

Cyanuret of mercury is also formed by boiling peroxide of mercury in solution of ferrocyanuret of potassium. When cyanuret of mercury is boiled in water with peroxide of mercury, a compound which forms small granular crystals, consisting of cyanuret and oxide of mercury, is obtained; hence, in making the cyanuret by the above process, excess of mercurial oxide should be avoided.

Cyanuret of mercury consists of

		Gay Lussac.	Porrett.
Mercury . . . . .	1 . . . . .	200 . . . . .	79.25 . . . . .
Cyanogen . . . . .	2 . . . . .	52 . . . . .	20.75 . . . . .
	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	1	252	100.00
		100.00	100.00

When cyanuret of mercury and iodide of potassium are mixed together in solution, pearly crystals are thrown down, which, when redissolved and crystallized, form large thin and brilliant plates, requiring 16 parts of water at 60° for their solution. When strongly heated they are decomposed, leaving a residue of iodide of potassium blackened with charcoal. (*Ann. de Chim. et Phys.*, xix., 220.)

FULMINATING MERCURY; FULMINATE OF MERCURY. This compound was discovered by Mr. Howard. (*Phil. Trans.*, 1800, p. 214.) It is prepared by dissolving 100 grains of mercury in a measured ounce and a half of nitric acid, aided by heat. This solution is to be poured, when cool, into two measured ounces of alcohol in a glass basin, and gently warmed: it soon begins to effervesce and evolve ethereal vapour, and if the action is too violent, it must be quelled by cooling the vessel, or by the addition of a little cold alcohol. During this action a yellow-gray precipitate falls, which is to be immediately separated by decantation and filtration, washed with small quantities of distilled water, and carefully dried at a heat not exceeding 212°. The above quantity of mercury yields about 120 grains of the powder when the operation has been most successful.

This compound, when heated to about 300°, explodes with a bright flame: it also detonates by friction, by the electric spark, and by contact of concentrated sulphuric and nitric acids: the gases evolved by its explosion are carbonic acid, nitrogen, and a little ammonia. Liebig and Gay Lussac have furnished some curious facts towards the history of this compound (*Ann. de Chim. et Phys.*, xxiv. and xxv.), showing that, like the corresponding *fulminating silver* (see SILVER), it consists of

Protoxide of mercury . . . . .	1	..	208	..	36
Cyanogen . . . . .	1	..	26	..	10.7
Oxygen . . . . .	1	..	8	..	3.3
	<hr/>		<hr/>		<hr/>
	1		242		100.0

FULMINIC ACID. According to Mr. E. Davy (*Trans. Dub. R. S.*, 1829), the peculiar modification, if so it may be termed, of cyanic acid, which constitutes a component of the above and analogous fulminating compounds, may be separated as follows. Put one part of fulminating mercury into a bottle with a ground stopper, together with two parts of clean zinc-filings, and about 20 parts of water: occasionally shake the mixture, and keep it at the temperature of about  $80^{\circ}$ , by which mercury will be separated, and a *fulminate of zinc* formed, the solution of which is to be filtered off and mixed with baryta-water (not in excess); this throws down oxide of zinc, and leaves *fulminate of baryta* in solution, which is to be decomposed by the careful addition of dilute sulphuric acid, and filtered: the filtered liquor is now a solution of *fulminic acid*: it is colourless, sweetish and astringent, of a pungent hydrocyanic odour, volatile, poisonous, and acid to tests: it throws down *fulminating mercury* and *fulminating silver*, from the protonitrate of mercury and the nitrate of silver. This acid, according to Mr. Davy, is not identical with the cyanic acid, but contains hydrogen, and is constituted of ( $2\text{ car} + 1\frac{1}{2}\text{ n} + \text{h} + \text{o}.$ )

SULPHOCYANURET OF MERCURY. When sulphocyanuret of potassium is mixed with protonitrate of mercury, a white precipitate falls. See Wöhler (*Gilb. Annalen*, lxi.), and Berzelius (*Lehrbuch*), in reference to these compounds.

BORATES OF MERCURY. When solution of protonitrate of mercury and of borate of soda are mixed and evaporated, small shining crystals of *protoborate of mercury* are obtained. Boracic acid occasions no precipitates in solution of pernitrate of mercury. The *Perborate of Mercury* has not been examined.

ARSENIATES OF MERCURY. Arsenic acid occasions a pale-yellow precipitate in solution of protonitrate of mercury, and a yellowish-white precipitate in solution of the pernitrate. Arsenious acid produces white precipitates in both solutions. These precipitates are soluble in muriatic acid.

MOLYBDIC ACID occasions a yellow precipitate in solution of protonitrate of mercury, easily soluble in nitric acid.

CHROMATE OF MERCURY. Chromate of potassa throws down an orange-coloured precipitate from the solutions of nitrate and pernitrate of mercury.

ALLOYS OF MERCURY. Mercury combines with most of the other metals, and forms a class of compounds which have been called *amalgams*. Many of these are definite and crystallizable compounds, and may be separated by gentle pressure, from the mercury in which the definite compound is suspended or dissolved. They are generally brittle or soft. One part of *potassium* with 70 of mercury produce a hard brittle compound. If mercury be added to the liquid alloy of *potassium and sodium*, an instant solidification ensues, and heat enough to inflame the latter metals is evolved. The use of an amalgam of *zinc* has already been adverted to for the excitation of electrical machines; and also of the

amalgam of *tin* for silvering looking-glasses\*. The amalgams of *gold* and *silver* are employed in gilding and plating. An amalgam of two parts of *mercury*, one of *bismuth*, and one of *lead*, is fluid, and when kept for some time deposits cubic crystals of bismuth. *Amalgam of copper* may be made as follows: To a hot solution of sulphate of copper, add a little muriatic acid and a few sticks of zinc, and boil the mixture for about a minute: by this means the copper will be precipitated in a metallic state, and in a finely-divided spongy form: take out the zinc, pour off the liquor, wash the copper with hot water, and pour upon it a little dilute nitrate of mercury, which will instantly cover every particle of copper with a coating of mercury: then add mercury to the amount of two or three times the weight of the copper, and a slight trituration will combine them so far that the completion of the process may be effected by heating the mixture for a few minutes in a crucible. (Aikin's *Dictionary*, Art. MERCURY.) *Antimony* and *tellurium* combine difficultly with mercury into granular compounds. Amalgam of *arsenic* was obtained by Bergman by digesting one part of powdered arsenic with five of quicksilver, and frequently agitating the mixture.

AMALGAM OF AMMONIA; METALLIZATION OF AMMONIA. When mercury is negatively electrized in a solution of ammonia, or when an amalgam of potassium and mercury is placed upon moistened muriate of ammonia, the metal increases in volume, and becomes of the consistency of butter, an appearance which has sometimes been called the *metallization of ammonia*. The compound appears only to contain ammonia and mercury, though its real nature has not been satisfactorily ascertained. It has suggested some hypotheses concerning the nature of ammonia and the metals, which are scarcely worth recording. Upon this subject, however, the reader may consult Gay Lussac and Thenard (*Recherches Physico-Chimiques*, vol. i.), who, finding the amalgam resolvable into mercury, ammonia, and hydrogen, regard it merely as a compound of those substances; and Berzelius (*Lehrbuch*, i.), who considers the appearances as resulting from the combination of a metal, which he terms *ammonium*, with the mercury.

\* This beautiful process is performed as follows: A single and perfect sheet of tinfoil, of proper thickness, and somewhat larger than the plate of glass, is spread upon a perfectly plane table of slate or stone; mercury is then poured upon it, and rubbed upon its surface by a hare's foot, or a ball of flannel or cotton, so as to form a clean and bright amalgam; upon this, excess of mercury is poured, till the metal has a tendency to run off: the plate of glass, previously made perfectly clean, is then brought horizontally towards the table, and its edge so adjusted, as, by gradually and steadily sliding it forward, to displace some of the excess of mercury, and float the plate as it were over the amalgam, the dross upon its surface being pushed onwards by the edge of the glass, so that the mer-

cury appears beneath it with a perfectly uniform, clean, and brilliant reflecting surface: a number of square weights, of 10 or 12 lbs. each, are now placed side by side upon the surface of the plate, so as entirely to cover it, and press it down upon the amalgamated surface of the tin; in this way the excess of mercury is partly squeezed out, and the amalgam is made to adhere firmly to the glass. The mercury, as it runs off, is received into a channel on the side of the table, which is slightly inclined to facilitate the drainage, and in about 48 hours the weights are taken off and the plate is carefully lifted from the table and set nearly upright, by which the adhering mercury gradually drains off, and the solid crystalline amalgam remains perfectly and uniformly adhering to the glass.

CHARACTERS OF THE SALTS OF MERCURY. The soluble salts of the *protoxide* are mostly white, of a metallic taste, and not virulently active as poisons. Some of them, when neutral, are resolved by water into basic and acid salts. Phosphorous and sulphurous acids, and protochloride of tin, precipitate metallic mercury: the caustic alkalis throw down a black powder; the carbonated alkalis, yellow or brown; the phosphates white, even in very dilute solutions; sulphuretted hydrogen and the hydrosulphurets, black; hydriodic acid and the iodides yellow; muriatic acid and the chlorides, white and curdy; the alkaline chromates, scarlet; ferrocyanuret of potassium, white; the oxalates white, even when very dilute; tincture of galls, brownish-yellow. The soluble salts of the *peroxide* of mercury are mostly white when neutral, yellow when basic; they are poisonous, and nauseously metallic to the taste, and are often resolved by water into acid and basic salts. Copper throws down from them metallic mercury, and ammonia and carbonate of ammonia produce white precipitates; iodide of potassium a scarlet-red; and infusion of galls an orange precipitate. Unless in concentrated solution they are not affected by muriatic or oxalic acids. The presence of organic substances interferes considerably with the appearances produced by some of the above tests; hence, in cases of poisoning by corrosive sublimate, peculiar precautions are sometimes required, and in all cases the precipitate should be collected and heated in a tube, if necessary, with a little white flux, or some such reducing agent, so as to separate metallic mercury, the microscopic globules of which are easily sublimed and discerned. (See Christison *on Poisons*, and Rose's *Analytical Chemistry*.) The insoluble mercurial salts are mostly volatilized at a red-heat, and they are all decomposed, with the production of metallic mercury, when mixed with a little carbonaceous matter, and heated in a glass tube.

### § XXX. SILVER.

THIS metal, the *Luna* or *Diana* of the alchemists (☽), was known at a very remote period; it is mentioned in the book of Job: it is found *native*, and in a variety of combinations; the most common of which is the *sulphuret*.

*Native Silver* has the general characters of the pure metal. It occurs in masses; arborescent; capillary; and, sometimes, crystallized in cubes and octoëdra. It is seldom pure, but contains small portions of other metals, which affect its colour and ductility. It is chiefly found in primitive countries. In Peru and Mexico are the richest known mines of native silver. The mines of Saxony, Bohemia, and Swabia, and those of Kongsberg in Norway, are the richest in Europe. It has been found in Cornwall and Devonshire.

*Pure Silver* may be procured by dissolving the standard silver of commerce in pure nitric acid, diluted with an equal measure of water. Immerse a plate of clean copper into the solution, which soon occasions a precipitate of metallic silver; collect it upon a filter; wash it with solution of ammonia, and then with water, and fuse it into a button.

It may also be procured by adding to the above solution of standard silver, a solution of common salt; collect, wash, and dry the precipitate,

and gradually add it to twice its weight of fused carbonate of potassa in a red-hot crucible. Metallic silver is separated, and may be fused into a button.

Silver has a pure white colour, and considerable brilliancy. Its specific gravity is 10.5. It is so malleable and ductile, that it may be extended into leaves not exceeding a ten-thousandth of an inch in thickness, and drawn into wire finer than a human hair. Silver melts at a bright red-heat, estimated by Mr. Daniell at 1873° of Fahrenheit's scale, and when in fusion appears extremely brilliant. It resists the action of air at high temperatures for a long time, and does not oxidize; the *tarnish* of silver is occasioned by sulphureous vapours; it takes place very slowly upon the pure metal, but more rapidly upon the alloy with copper used for plate, and was found by Proust to consist of sulphuret of silver. Pure water has no effect upon the metal; but if the water contain vegetable or animal matter, it often slightly blackens its surface in consequence of the presence of sulphur. If an electric explosion be passed through fine silver-wire, it burns into black powder, which is an oxide of silver. In the Voltaic circle it burns with a fine green light, and throws off abundant fumes of oxide. Exposed to an intense white-heat, it boils and evaporates. If suddenly cooled, it crystallizes during congelation, often shooting out like a cauliflower, and throwing small particles of the metal out of the crucible. This arises, according to Lucas, from the sudden escape of oxygen, which the metal absorbs and retains whilst fluid, but suddenly gives it off when it solidifies: this property of absorbing oxygen is prevented by the presence of a quantity of copper, not exceeding 5 *per cent*.

The analyses of the compounds of silver furnish data from which its equivalent may be estimated at 108, (108 Gmelin and Turner; 110 Thomson.) In the table at page 317, I have placed its equivalent at 110, a number which, it will be seen, closely agrees with many of the best analyses; but the experiments of Berzelius, Turner, and Phillips, indicate a somewhat lower equivalent, and, in conformity with their results, I have adopted the number 108.

**REDUCTION OF SILVER ORES.** Silver is not unfrequently obtained in considerable quantities from *argentiferous sulphuret of lead*, which is reduced in the usual way, and the argentiferous lead is then fused in a shallow dish, placed in a reverberatory furnace, with a current of air constantly passing over its surface; in this way the lead is converted into *litharge*, and the silver, not being thus oxidized, is left in the metallic state; it is fused in a porous crucible, called a *cupel* or *test*, by which the remaining lead is entirely separated, and a button of pure silver remains. The litharge which results from this operation is afterwards itself reduced by charcoal, and furnishes lead which is perfectly free from silver, the ordinary lead of commerce generally containing a trace of the latter metal. Some of the silver ores, especially the *sulphurets*, are reduced by *amalgamation*. The ore, when washed and ground, is mixed with a portion of common salt and roasted: during this operation sulphate of soda and chloride of silver are formed: the product is then powdered, and agitated with mercury, water, and filings or fragments of iron; in this operation the chloride of silver is decomposed, chloride of iron is formed which is washed away, and the silver and mer-

cury combine into an amalgam, from which the excess of mercury is first squeezed out in leather bags, and the remainder driven off by distillation. The old process of *eliquation* is now scarcely used: it consisted in fusing alloys of copper and silver with lead; this triple alloy was cast into round masses, which were set in a proper furnace upon an inclined plane of iron with a small channel grooved out, and heated red-hot, during which the lead melted out, and, in consequence of its attraction for silver, carried that metal with it, the copper being left behind in a reddish-black spongy mass. (Aikin's *Dictionary*, Art. SILVER.)

OXIDE OF SILVER ( $ag + o$ ) may be obtained by adding baryta-water, or dilute solution of potassa, to the solution of nitrate of silver, and washing the precipitate. It is of a dark olive-colour, tasteless, insoluble in water, and, when gently heated, is reduced to the metallic state. Long exposure to light also reduces it, converting it into a black powder, which is either silver or its suboxide. It confers a yellow colour upon glass, and is employed in enamel and porcelain painting. Its specific gravity is 7.14 (Herapath). It consists of

						Berzelius.	Davy.	Gay Lussac and Thenard.			
Silver	1	..	108	..	93.103	..	93.112	..	93.1	..	92.937
Oxygen	1	..	8	..	6.897	..	6.888	..	6.9	..	7.063
	1		116		100.000		100.000		100.0		100.000

This is apparently the only *salifiable* oxide of silver; but Mr. Faraday has rendered it probable that there is another combination of silver and oxygen, containing a smaller proportion of oxygen than the above, which may be called a *suboxide*. He obtained it in the form of a black film, by exposing an ammoniacal solution of oxide of silver to the air (*Quar. Jour.*, v., 368). Ritter, by electrizing a weak solution of silver, observed the deposition of acicular crystals at the positive pole, which, according to Grothuss, dissolve in nitric acid, without decomposition, and are a *peroxide of silver*. Ammonia energetically decomposes this compound, and sulphuric and phosphoric acids convert it into the protoxide.

AMMONIURET OF SILVER; ARGENTATE OF AMMONIA. Oxide of silver readily dissolves in ammonia, and by particular management, a *fulminating silver*, composed of the oxide combined with ammonia, may be obtained. It was discovered by Berthollet. (*Ann. de Chim.*, i.) The best process for obtaining it is to pour a small quantity of liquid ammonia upon the oxide; a portion is dissolved, and a black powder remains, which is the detonating compound. It explodes when gently heated; nitrogen and water are instantaneously evolved, and the silver is reduced. The oxide of silver should be perfectly pure and thoroughlyedulcorated, and the ammonia quite free from carbonic acid. It should only be prepared in small quantities, and handled with the greatest caution, many accidents having arisen from its careless management. It sometimes explodes while still wet.

CHLORIDE OF SILVER. ( $ag + c$ .) This compound is easily procured by adding a solution of chlorine, of muriatic acid, or of common salt, to a solution of nitrate of silver, or, indeed, to any of the soluble salts of silver, with the exception of the hyposulphite. It falls in the form of a heavy tasteless powder, of a white colour, but which, by exposure to light,



becomes brown, and ultimately black. It is perfectly insoluble in water; so that the minutest portion of muriatic acid, or of a chloride in solution, may be detected by adding to the liquid a drop or two of nitrate of silver; it becomes opalescent and brown by exposure to light. It is very sparingly dissolved by concentrated muriatic acid, and thrown down upon dilution. When dry chloride of silver is heated to dull-redness in a silver crucible it does not lose weight, but fuses, and, on cooling, concretes into a gray semitransparent substance, (sp. gr. 5.45,) which has been called *horn silver*, or *luna cornea*. If slowly cooled, Proust has remarked that it has a tendency to octoëdral crystallization. Heated to a bright red or white heat in an open vessel, it volatilizes in dense white fumes. Scheele was the first who examined the cause of the blackening effect of light upon this chloride, and the curious results of his researches have already been referred to (page 184). He found that the metal was partially reduced, and muriatic acid formed; hence moisture is necessarily present. Seebeck found that white chloride of silver might be exposed, without change of colour, when covered in a stopped phial, with sulphuric acid; but if the phial was open, the blackening ensued; as it did also when water was added. Common hydrogen gas, and substances affording hydrogen, decompose moist chloride of silver: they reduce it to the metallic state, and the chlorine is carried off in the form of muriatic acid; but in the dark, perfectly pure hydrogen does not discolour the chloride.

If fused with twice its weight of potassa or soda, chloride of silver is decomposed, and a globule of metallic silver is obtained. This reduction is best effected by projecting the dry chloride upon twice its weight of fused carbonate of potassa, or upon the fused mixture of the carbonates of potassa and soda. It is also rapidly decomposed when moist, by tin and zinc, and by many of the other metals, especially if a little muriatic acid be added. Triturated with zinc-filings and moistened, the heat produced is so considerable as to fuse the resulting alloy of zinc and silver. (Faraday, *Quarterly Journal of Science and Arts*, viii., 374.)

Chloride of silver is very soluble in ammonia, a circumstance by which it is usefully distinguished from some other chlorides, which, like it, are white, and formed by precipitation. We should be cautious in applying heat to the ammoniacal solution, as it sometimes forms a precipitate of fulminating silver. The ammoniacal solution furnishes crystals, which, when exposed to air, or put into water, lose their transparency, ammonia is evolved, and they crumble into chloride of silver. The fused chloride, exposed to ammoniacal gas, absorbs a considerable portion, which is given off by heat. If the dry chloride, thus saturated with ammonia, be thrown into chlorine, the ammonia spontaneously inflames. (Faraday, *Journal of Science and Arts*, vol. v., p. 75.) Chloride of silver is soluble in and decomposed by all the liquid hyposulphites.

As chloride of silver is insoluble in water, and very readily formed, it is often employed in quantitative analysis, as a means of ascertaining the proportion of chlorine present in various compounds. In these cases some excess of the precipitant should be used, and the precipitate allowed to subside previous to separating it upon the filter: if the supernatant liquor become perfectly clear, the whole of the silver has fallen; if it

remain opalescent, a portion is probably still retained. When the precipitate remains long suspended, its deposition may be accelerated by heat, or by adding a little nitric acid. The chloride in these cases should be perfectly dried in a silver crucible, up to incipient fusion.

Chloride of silver consists of

			Bucholz.	Rose.	Wenzel and Berzelius.	Gay-Lussac.	Marcet and J. Davy.	Turner.	
Silver	1	. 108	. 75	. 75	. 75.18	. 75.33	. 75.25	. 75.5	. 75.3
Chlorine	1	. 36	. 25	. 25	. 24.82	. 24.67	. 24.75	. 24.5	. 24.7
	<u>1</u>	<u>144</u>	<u>100</u>	<u>100</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.0</u>	<u>100.0</u>

*Native Chloride of Silver* has been found in most of the silver-mines; it occurs massive and crystallized in small cubes and octoëdra.

CHLORATE OF SILVER ( $Ag + Cl'$ ) is formed by digesting oxide of silver in chloric acid: it forms small rhombic crystals, which, by the action of chlorine, are converted into chloride of silver. They are soluble in four parts of water at  $60^\circ$ . (Chenevix, Vauquelin.)

IODIDE OF SILVER ( $ag + i$ ) is precipitated upon adding hydriodic acid, or a soluble iodide, to a solution of nitrate of silver. It is of a greenish-yellow colour, insoluble in water, and decomposed when heated with potassa. It is particularly characterized by being insoluble in ammonia. When fused it acquires a red-colour. It volatilizes before the blowpipe, leaving a little silver only behind. Concentrated nitric and sulphuric acid decompose it. It dissolves in concentrated solutions of the alkaline chlorides, and combines with iodide of potassium. It has been found *native* in Mexico, associated with galena. It consists of

Silver	. 1	..	108	..	46.3
Iodine	. 1	..	125	..	53.7
	<u>1</u>		<u>233</u>		<u>100.0</u>

IODATE OF SILVER ( $Ag + i'$ ) is precipitated in the form of a white powder by adding iodic acid or iodate of potassa to a solution of nitrate of silver. It is very soluble in ammonia. It is decomposed by sulphurous acid, which throws down iodide of silver, and becomes sulphuric acid.

BROMIDE OF SILVER ( $ag + b$ ) is an insoluble yellowish substance thrown down upon the addition of bromine, or hydrobromic acid, or the soluble bromides, to nitrate of silver. It dissolves in ammonia. (Balard, *Ann. de Chim. et Phys.*, xxxii. 361.)

BROMATE OF SILVER, not described.

FLUORIDE OF SILVER ( $ag + f$ ) is a soluble compound, which does not crystallize. When heated it fuses; and at a higher temperature, and exposed to air, it is slowly reduced. (Berzelius; *Ann. de Chim. et Phys.*, xi., 121.)

NITRATE OF SILVER. ( $Ag + n'$ ) Nitric acid, diluted with three parts of water, readily dissolves silver, with the disengagement of nitric oxide gas. If the acid contain the least portion of muriatic, the solution will be turbid, and deposit a white powder; and if the silver contain copper, it will have a permanent blueish hue; or if gold, that metal will remain undissolved in the form of a black powder.

The solution of nitrate of silver should be perfectly clear and colourless; it is caustic, and tinges animal substances of a deep yellow, which, by exposure to light, becomes a deep purple, or black stain, and is indelible, or peels off with the cuticle: it consists of reduced silver. Nitrate of silver may be obtained in white anhydrous crystals, in the form of four and six-sided tables or thin plates: by slow evaporation it forms right rhombic prisms. (Brooke, *Ann. of Phil.*, 2nd series, vii. 162.) They have a bitter and metallic taste, and are soluble in about their own weight of water at 60°. Alcohol also dissolves about one-fourth its weight of this salt, at its boiling-point, but deposits nearly the whole as it cools. According to Proust (Nicholson's *Journal*, xv. 376), a solution of this nitrate, when boiled with finely-divided silver, dissolves a portion, and yields a solution containing a suboxide of silver.

Nitrate of silver blackens when exposed to light, and when thus acted upon, is no longer perfectly soluble in water, owing to the separation of a portion of metallic silver. When heated in a silver crucible it fuses into a grey mass, and if cast into small cylinders, forms the *lapis infernalis*, or *lunar caustic* of pharmacy; the *argenti nitras* of the *Pharmacopœia*. In forming this preparation, care should be taken not to overheat the salt, so as to blacken it, and the moulds should be warmed. Exposed to a red-heat, the acid is partly evolved and partly decomposed, and metallic silver obtained. Sulphur, phosphorus, charcoal, hydrogen, and several of the metals, decompose this nitrate. A few grains mixed with a little sulphur, and struck upon an anvil with a heavy hammer, produce a detonation; phosphorus occasions a violent explosion when about half a grain of it is placed upon a crystal of the nitrate, upon an anvil, and struck sharply with a hammer; and if heated with charcoal it deflagrates, and the metal is reduced.

If a piece of silk dipped into a solution of nitrate of silver be exposed, while moist, to a current of hydrogen gas, it is first blackened, and afterwards becomes iridescent from the reduction of portions of the metal. (Mrs. Fulhame's *Essay on Combustion*.) Ivory, marble, and several other bodies, may be stained black, or even silvered, by soaking them in a solution of nitrate of silver, and fully exposing them to the action of the sun's rays. When the vapour of pure distilled water is made to pass through nitrate of silver, the solution assumes all the shades between yellow and dark-brown, according to its concentration and the time the steam has passed through it. When it has acquired the temperature of 212°, its colour increases rapidly. Nitric acid immediately destroys this colour, the cause of which is referred by Professor Pfaff to the deoxidizing agency of the steam. (*Quarterly Journal*, xvi. 162.) A stick of phosphorus, introduced into a solution of nitrate of silver, soon becomes beautifully incrustated with the metal, which separates upon it in arborescent crystals. A plate of copper occasions a brilliant precipitation of silver, and the copper is oxidized and dissolved by the acid. Mercury introduced into the solution of nitrate of silver, causes a beautiful crystalline deposit of silver, called the *arbor Dianæ*: it was first remarked by Lemery. To obtain this crystallization in its most perfect state, the solution should contain a little mercury, and the mercury put into it should be alloyed with a little silver. Baumé directs an amalgam of one

part of silver with seven of mercury, of which a small piece is to be introduced into a solution composed of six drachms of saturated nitrate of silver and four drachms of a similar solution of mercury diluted with five ounces of distilled water: a small flask or matrass should be used for the experiment, kept perfectly at rest: in a few minutes small filaments of silver darken the surface of the amalgam, and in about eight and forty hours the whole has separated in a shrub-like form. The addition of mercury to the solution, and of silver to the precipitating mercury, is said to give a degree of tenacity to the arborescent deposit of crystals, which prevents their falling to the bottom of the flask.

The alkaline metallic oxides decompose nitrate of silver; it is also decomposed by muriatic, sulphuric, phosphoric, and boracic acids. The protosulphate of iron throws down metallic silver when added to a solution of the nitrate: protochloride of tin forms a gray precipitate consisting of peroxide of tin and oxide of silver. Ammonia, added to solution of nitrate of silver, occasions a precipitate, soluble in excess of the alkali. (See Berthollet's Fulminating Silver, p. 802.)

Nitrate of silver is employed for writing upon linen under the name of *indelible* or *marking ink*, which may be prepared by dissolving two drachms of pure nitrate of silver and one drachm of gum arabic in seven drachms of distilled water, coloured by a little China ink. The preparatory liquid for moistening the cloth is made by dissolving two ounces of crystallized carbonate of soda and two drachms of gum arabic in four ounces of water. Nitrate of silver is an ingredient in some of the liquids which are sold for the purpose of changing the colour of hair. It is used in medicine; and in surgery, as an excellent caustic. When taken internally, a very disagreeable effect frequently follows its use, which is the discoloration of the *rete mucosum*; so that the whole surface of the body, and especially the parts most exposed to light, acquire a leaden-gray or livid colour, which is permanent, and can neither be removed nor prevented.

Solution of nitrate of silver is a valuable test of the presence of chlorine, muriatic acid, and the soluble chlorides, with which it forms a white cloud when very dilute, but a flaky precipitate when more concentrated; the precipitate is soluble in ammonia. Heat, agitation, or the addition of a few drops of nitric acid, so as to render the liquid sour, facilitate the deposition of the precipitate. The hydriodic, hydrobromic, and hydrocyanic acids, also occasion white precipitates in solution of nitrate of silver, which blacken by exposure to light. Its application as a test for arsenic and arsenious acids has already been noticed. Gallic and tannic acid, and the varieties of extractive matter, discolour nitrate of silver without the aid of light. A peculiar extractive matter sometimes occurs in rough nitre, which also causes its solution to blacken nitrate of silver. Some spring and mineral waters contain a substance producing a similar effect.

Nitrate of silver is an anhydrous salt, composed of

Oxide of silver . . . . .	1	..	116	..	68.23	..	Proust.
Nitric acid . . . . .	1	..	54	..	31.77	..	69.5
	<hr/>		<hr/>		<hr/>		30.5
	1		170		100.00		100.0

By long digestion of powdered silver in nitric acid already saturated with the metal, a salt is obtained which is regarded as a *hyponitrite of silver*. It is more soluble than the nitrate, and difficultly crystallizable. It is the same salt as that which Proust regarded as a nitrate of a suboxide: and it appears not improbable that it may contain a suboxide. (See p. 802.)

SULPHURET OF SILVER. (*ag + s.*) Silver readily combines with sulphur, and produces a gray crystallizable compound, considerably more fusible and much softer than silver. It may be obtained by heating finely-divided silver or plates of silver with sulphur.

Sulphuretted hydrogen and hydrosulphuret of ammonia occasion a copious black precipitate of sulphuret of silver when added to solutions of the metal: sometimes a portion of the silver is apparently at the same time reduced to the metallic state. It is the presence of some form of sulphur, generally sulphuretted hydrogen, which occasions the tarnish upon silver, and which, though only superficial, is a great obstacle to many applications that might otherwise be made of this beautiful metal. Sulphuret of silver consists of

						Vauquelin.	Berzelius.	Wenzel.	
Silver . . .	1	. . .	108	. . .	87.1	. . .	87.27	. . .	85.5
Sulphur . . .	1	. . .	16	. . .	12.9	. . .	12.73	. . .	14.5
	1		124		100.0		100.00		100.0

*Native Sulphuret of Silver*, or *vitreous silver-ore*, is found in various forms, and when crystallized, is in cubes, octoëdra, and dodecaëdra. It is soft and sectile. The finest specimens are from Siberia. The method of its reduction has been above described. A triple combination of *silver, antimony, and sulphur*, constitutes the *red or ruby silver-ore*; it is found massive and crystallized in hexaëdral prisms. It consists of about 70 parts of sulphuret of silver, and 30 sulphuret of antimony; or, according to Bonsdorff, of 3 atoms of silver, 2 of antimony, and 6 of sulphur. It occurs in all the silver-mines, and is sometimes accompanied by the *brittle sulphuret of silver*, or *silver glance*, and by *antimonial silver*. ( $2 ag + an.$ )

HYPOSULPHITE OF SILVER ( $Ag + \underline{S}$ ) has been examined by Herschel. (*Edin. Phil. Journal*, i. 26.) It is formed by dropping a weak solution of nitrate of silver into a very dilute solution of hyposulphite of soda: a white cloud is at first produced, which redissolves on agitation; on adding more of the precipitant, the cloud re-appears and aggregates into a gray precipitate, which appears to consist of hyposulphite of silver; the supernatant liquor tastes intensely sweet, which is remarkable, considering the disgusting bitterness both of the nitrate and of the hyposulphite, and shows, "how little we know of the way in which bodies affect the organs of taste. Sweetness and bitterness, like acidity, seem to depend upon no particular principle, but to be regulated by the state of combination in which the same principles exist at different times." Hyposulphite of silver is also produced when chloride of silver is dissolved in any of the hyposulphites; the solution is intensely sweet without any metallic flavour. These facts show the strong affinity that exists between oxide of silver and hyposulphurous acid.

HYPOSULPHITE OF POTASSA AND SILVER is formed when liquid potassa is dropped into the solution of chloride of silver in hyposulphite of soda; it separates in the form of a copious precipitate, which, when washed and dried, is found to consist of small gray pearly scales; they are difficultly soluble in water; of a very sweet taste; and, heated before the blowpipe, afford a bead of silver. Several other analogous double salts have been described by Herschel.

SULPHITE OF SILVER ( $Ag + \bar{S}$ ) is obtained in crystalline grains by digesting oxide of silver in sulphurous acid, or by adding an alkaline sulphite to a solution of silver. It produces double salts with the sulphites of the alkalis. According to Fourcroy, it is not blackened by exposure to light, nor altered by air.

HYPOSULPHATE OF SILVER ( $Ag + \underline{S}'$ ) is formed by digesting carbonate of silver in hyposulphuric acid: it crystallizes in permanent prismatic crystals, soluble in two parts of cold water, and contains two proportionals of water of crystallization. Excess of ammonia added to a solution of this salt occasions a gradual precipitation of crystalline grains, consisting of an *ammonio-hyposulphate of silver*. (Heeren.)

SULPHATE OF SILVER ( $Ag + S'$ ) is deposited when sulphate of soda is mixed with nitrate of silver. It is also formed by boiling silver with its weight of sulphuric acid. It forms a white saline mass, easily fusible. It requires about 90 parts of water at  $60^\circ$  for its solution; in boiling water it is more soluble, and is deposited, as the solution cools, in small anhydrous prismatic crystals: it is decomposed at a red-heat, and leaves metallic silver.

Upon the large scale, small portions of gold may be most economically separated from large quantities of silver, by heating the finely-granulated alloy in sulphuric acid: the gold remains in the form of a black powder, and the sulphate of silver may be decomposed by the action of metallic copper; the silver is precipitated in a pulverulent state, and, with a little borax or other vitrifiable flux, is fused, and cast into ingots; the sulphate of copper is easily obtained in the crystallized state by evaporating the residuary liquid.

A compound acid, which may be called *nitro-sulphuric*, consisting of one part of nitre dissolved in about ten of sulphuric acid, dissolves silver at a temperature below  $200^\circ$ , and the solution admits of moderate dilution before sulphate of silver separates from it. This acid scarcely acts upon copper, lead, or iron, unless diluted with water; it is, therefore, useful in separating the silver from old plated articles; the precious metal may afterwards be separated either in the form of chloride, by adding common salt; or by diluting the acid and continuing the immersion of the pieces of copper which have lost their silvering, and which will now dissolve in the diluted acid, and occasion the precipitation of metallic silver. (Keir, *Phil. Trans.*, lxxx.)

Sulphate of silver consists of

Oxide of silver . . .	1	..	116	..	74.3
Sulphuric acid . . .	1	..	40	..	25.7
	<hr/>		<hr/>		<hr/>
	1		156		100.0

PHOSPHURET OF SILVER (*ag + p*) is a white brittle compound; it is formed either by projecting phosphorus upon red-hot silver, or by heating a mixture of 1 part of silver-filings, 2 of vitrified phosphoric acid, and 0.5 of charcoal. It loses its phosphorus when fused and exposed to air.

PHOSPHATE OF SILVER. When the neutral phosphate of soda is added to nitrate of silver, a yellow anhydrous precipitate falls, which is fusible at a white-heat, and soluble in nitric acid, and in phosphoric acid, and quickly discoloured by exposure to light: its specific gravity is 7.3: when heated it becomes brown, but regains its yellow tint as it cools. It consists of

						Berzelius.
Oxide of silver . . .	1½	..	174	..	82.86	.. 82.975
Phosphoric acid . . .	1	..	36	..	17.14	.. 17.025
	1		210		100.00	100.000

When this salt is dissolved in phosphoric acid, a part of it is deposited in granular crystals, and by spontaneous evaporation of the residuary solution, white plumose crystals, probably of the neutral phosphate of silver, are deposited\*.

Neither HYPHOSPHITE nor PHOSPHITE OF SILVER have been examined: probably oxide of silver would be reduced by these acids.

SELENIURET OF SILVER (*ag + se*) obtained by precipitating nitrate of silver by seleniuretted hydrogen, is a black powder, which fuses into a globule having a metallic lustre. It consists of of 73.16 silver, 26.84 selenium. When silver is fused with selenium, a gray *biseleniuret* is formed, from which excess of selenium is expelled by heat. (Berzelius.)

SELENITE OF SILVER is thrown down, in the form of a white powder, very sparingly soluble in hot water. It is fusible, and at a high heat gives out selenious acid and oxygen, and leaves metallic silver. It is not discoloured by exposure to daylight.

CARBONATE OF SILVER is precipitated in the form of a white insoluble powder, by adding carbonate of potassa to nitrate of silver. It blackens by exposure to light. Carbonate of ammonia only throws down a portion of the silver from the nitrate, and forms a triple *ammonio-carbonate of silver*.

BORATE OF SILVER is thrown down from the nitrate of silver in the form of a white crystalline powder, by adding solution of boracic acid. It is very difficultly soluble in water.

CYANURET OF SILVER. (*ag + cy*.) Hydrocyanic acid causes a white precipitate in solution of nitrate of silver, which is *cyanuret of silver*, and which, when heated, fuses, and, at a high temperature, gives out cyanogen. It is insoluble in water, but readily soluble in ammonia. It is easily decomposed by muriatic acid, and by sulphuretted hydrogen; but sulphuric and nitric acids scarcely act upon it unless concentrated and heated.

ARGENTO-CYANURETS. Cyanurets of the alkaline bases form soluble double salts with cyanuret of silver; they are insoluble in alcohol, which throws them down from their aqueous solutions. The *argento-cyanuret of potassium* yields plumose colourless crystals: it produces precipitates

\* In reference to *pyrophosphate of silver* see pp. 445 and 583.

in many of the metallic solutions, which are *insoluble argento-cyanurets*, corresponding in composition with the ferrocyanurets.

SULPHOCYANURET OF SILVER falls in the form of a white curdy precipitate when sulphocyanuret of potassium is added to nitrate of silver. It slowly blackens by exposure to light.

CYANATE OF SILVER. When cyanate of potassa is added to nitrate of silver a white powder falls, somewhat soluble in hot water, and soluble in ammonia; it blackens when heated, and burns with deflagration.

FULMINE OF SILVER; FULMINATING SILVER of *Brugnatelli and Howard*. This curious and dangerous compound is prepared as follows: 100 grains of fused and finely-powdered nitrate of silver are added to an ounce of warm alcohol, and the mixture stirred in a sufficiently large glass basin; an ounce of fuming nitric acid is then added, and presently a violent effervescence ensues: a powder falls; as soon as this appears white, cold water is added, and the powder is immediately to be collected upon a filter, washed, and carefully dried at a temperature of  $212^{\circ}$ . In collecting and handling this powder, the utmost caution is requisite; it should be made in small quantities only, and touched with nothing hard, for it has sometimes exploded upon the contact of a glass rod, even under water: the feather of a common quill serves to collect it; and it should be kept in a wide-mouthed vessel covered by paper, and by no means in a stoppered or even a corked phial, as many serious accidents have arisen from its sudden and unexpected explosion. In short, one cannot be too careful in meddling with it, and its use for fulminating balls and for other purposes of amusement is highly dangerous.

Berzelius observes, that in preparing fulminating silver, a vessel of sufficient capacity should be used to prevent the liquid running over during the effervescence, by which portions of the powder are deposited upon its exterior, and apt to explode when dry; that all approach of flame should be avoided during the escape of the nitrous etherized gas, because its inflammation would probably occasion the powder to explode; and that care should be taken to avoid introducing all hard substances to stir or touch the precipitate.

Liebig's process for the preparation of fulminating silver differs a little from the above, and is as follows: A drachm of refined silver is dissolved in half an ounce of nitric acid, specific grav. 1.52; two ounces of alcohol, specific gravity 0.85, are then added, and the whole heated in a matrass; white flocculi soon appear, and when ebullition begins, the heat is to be withdrawn; the effervescence, however, continues, and the powder falls; when action ceases, the powder is to be collected with the precautions above described.

Fulminating silver acquires a dingy hue by exposure to light; it dissolves in about 40 parts of boiling water, and as the solution cools, it is deposited in minute crystals. It detonates in the quantity of a grain, or even half a grain, with great violence, when heated, or touched by any hard body: placed upon a piece of rock-crystal, and touched in the slightest manner by another crystal, it explodes violently; upon the contact of sulphuric acid, and by the electric spark, it also detonates. The nature of this substance has been investigated by Liebig and Gay Lussac (*Ann. de Chim. et Phys.*, xxiv. and xxv.), who



have shown that it is a compound of oxide of silver with an acid having the same composition as the *cyanic acid*, and that the above fulminating product is, therefore, strictly speaking, a *cyanate of silver*, consisting of

				Gay-Lussac and Liebig.
Oxide of Silver . . . . .	1	..	116	.. 77.34
Cyanogen . . . . .	1	..	26	.. 17.33
Oxygen . . . . .	1	..	8	.. 5.33
	1		150	100.00
				77.528
				17.160
				5.312
				100.000

**BIFULMINATE OF SILVER** is produced by digesting the preceding in solution of potassa, filtering, and adding nitric acid; a precipitate falls, soluble in boiling water, from which crystals separate on cooling, composed of 2 atoms of acid, and 1 of oxide of silver, and which are dangerously explosive.

**FULMINATE OF POTASSA; ARGENTO-CYANATE OF POTASSA.** When solution of potassa (or other alkaline base) is digested with fulminating silver, half the oxide of silver is thrown down, and, on filtering and carefully evaporating the solution, white foliated crystals may be obtained, of a metallic taste, neutral to tests, soluble in 8 parts of boiling water, and not precipitated by chlorides. They explode by heat and friction. In this, and analogous compounds, therefore, the bifulminate of silver acts the part of an *acid* to the bases. (*argento-cyanic acid?*) This salt of potassa is composed of

Potassa . . . . .	1	..	48	.. 20.7	. . . . .	20.7
Oxide of silver . . . . .	1	..	116	.. 50.0	}	Argento-cyanic acid. } 79.3
Cyanic acid . . . . .	2	..	68	.. 29.3		
	1		232	100.0		100.0

*Fulminating mercury* is, as above stated, an analogous compound of protoxide of mercury and cyanic acid, and, when decomposed by the fixed alkalis, the mercury constitutes a part of the triple detonating salt, which may be called a *mercurio-cyanate*, or *fulminate*; and for mercury, some other metals may be substituted.

**ARSENITE OF SILVER** is precipitated in the form of a yellow powder, soon becoming gray and brown, by the addition of solution of arsenious acid to nitrate of silver. Nitrate of silver has already been adverted to as a test for white arsenic. (p. 759.)

**ARSENIATE OF SILVER** is thrown down from nitrate of silver by arsenic acid, of a reddish-brown colour. At a red-heat, this compound evolves oxygen; and arsenious acid, and arsenical silver remain.

**MOLYBDATE OF SILVER** and **TUNGSTATE OF SILVER** are precipitated in the form of white powder, insoluble in water.

**CHROMATE OF SILVER** is precipitated of a crimson-colour by adding chromate of soda to nitrate of silver. It soon loses its brilliant tint and becomes brown. It dissolves in nitric acid.

**ANTIMONIATE, TELLURATE, AND COLUMBATE OF SILVER**, are insoluble white powders.

**ALLOYS OF SILVER.** The compounds of this metal with potassium and sodium have not been examined. It unites difficultly with iron, and does not combine with cobalt, except in very small proportions. It combines with manganese, and readily with arsenic.

When silver and steel are fused together, an alloy is formed, which appears perfect while in fusion, but globules of silver exude from it on cooling, which shows the weak attraction of the metals. At a very high temperature the greater part of the silver evaporates, but a portion equal to about 1 in 500 remains, forming a perfect alloy, admirably adapted to the formation of cutting instruments. (Stodart and Faraday, on the Alloys of Steel, *Quarterly Journal*, ix.)

Silver readily combines with zinc and tin, forming brittle alloys. The alloy of silver with copper is of the most importance, as it constitutes plate and coin. By the addition of a small proportion of copper to silver, the metal is rendered harder and more sonorous, while its colour is scarcely impaired. The *standard silver* of this country consists of  $11\frac{2}{6}$  pure silver and  $\frac{1}{2}\frac{8}{0}$  copper, or 11.10 silver and 0.90 copper. A pound troy, therefore, is composed of 11 oz. 2 dwts. pure silver, and 18 dwts. of copper: it is coined into 66 shillings.

With lead the alloy is gray and brittle, as also with antimony, bismuth, cobalt, and arsenic.

Amalgam of silver is sometimes employed for *plating*; it is applied to the surface of copper, and the mercury being evaporated by heat, the remaining silver is burnished. The better kind of plating, however, is performed by the application of a plate of silver to the surface of the copper, which is afterwards beaten or drawn out. A mixture of chloride of silver, chalk, and pearlash, is employed for silvering brass: the metal is rendered very clean, and the above mixture, moistened with water, rubbed upon its surface. In this way thermometer scales and clock dials are usually silvered.

**ASSAY OF SILVER.** The analysis of alloyed silver is a very important process, and in continual practice by refiners and assayers. It may be performed in the humid way by dissolving the alloy in nitric acid, precipitating with muriatic acid, and either reducing the chloride by potassa in the way above described, or estimating the quantity of silver which it contains. The usual method, however, which is employed at the Mint, and by the refiners, is *cupellation*\*. Of the useful metals, there are three which are capable of resisting the action of air at high temperatures; these are silver, gold, and platinum; the others, under the same circumstances, become oxidized: it might, therefore, be supposed, that an alloy containing one or more of the first three metals, would suffer decomposition by mere exposure to heat and air, and that the oxidable metal would burn away. This, however, is not the case; for if the proportion of the latter be small, it is protected, as it were, by the former; or, in other cases, a film of infusible oxide coats the fused globule, and prevents the further action of the air. These difficulties are overcome by adding

\* Where great accuracy is requisite, the solution of the alloy, and the precipitation of the silver in the state of chloride, is the method that must be followed; but an experienced assayer will arrive at tolerably close results by cupellation, and where, as in the London Mint, many assays are often daily requisite, the humid process could not be adopted without serious interruption to the business of the establishment. Where, as in the French Mint, only one degree of fineness is to be estimated, the humid process, conducted with the *precautions* described by M. Gay Lussac, and with the aid of his apparatus, may be employed.

to the alloy some highly-oxidable metal, the oxide of which is *fusible*. Lead is the metal usually selected for this purpose, though bismuth will also answer. Supposing, therefore, that an *alloy of silver and copper* is to be *assayed*, or analyzed by *cupellation*, the following is the mode of proceeding: A clean piece of the metal, weighing about 20 grains, is laminated, and accurately weighed in a very sensible balance. It is then wrapped up in the requisite quantity of sheet-lead (*pure*, and reduced from litharge), apportioned by weight to the *quality* of the alloy under examination, and placed upon a small *cupel*, or shallow crucible made of bone-earth, which has been previously heated. The whole is then placed within the *muffle*, heated to bright-redness; the metals melt, and, by the action of the air which plays over the hot surface, the lead and copper are oxidized and absorbed by the cupel, and, if the operation has been skilfully conducted, a button of pure silver ultimately remains, the completion of the process being judged of by the cessation of the oxidation and motion upon the surface of the globule, and by the very brilliant appearance assumed by the silver when the oxidation of its alloy ceases. The button of pure metal is then suffered to cool gradually, and its loss of weight will be equivalent to the weight of the alloy which has been separated by oxidation, a certain allowance being made for a small loss of silver, which always occurs. To perform this process with the accuracy required at the Mint, certain precautions are requisite, which can only be learned by practice, so as to enable the operator to gain uniform results. An excellent article upon this subject will be found in Aikin's *Chemical Dictionary*, and in Mr. Children's *Translation of Thenard on Chemical Analysis*. (See also Vauquelin's *Manuel de l'Essayer*.)

CHARACTERS OF THE SALTS OF SILVER. The soluble salts of silver are recognised by furnishing a white precipitate with muriatic acid, which blackens by exposure to light, and which is readily soluble in ammonia; and by affording metallic silver upon the immersion of a plate of copper. The salts insoluble in water are mostly soluble in liquid ammonia, and, when heated on charcoal before the blowpipe, they afford a globule of silver.

Tin and lead are the most rapid precipitants of *metallic silver* from the nitrate: cadmium, zinc, copper, bismuth, and antimony, are more slow in their operation, and arsenic and mercury still more tardy. In all cases the silver appears crystallized; often blackish at first, but afterwards assuming the metallic lustre. Iron is a speedy reducer of the sulphate of silver. The insoluble salts of silver mixed with water are also similarly decomposed, but the operation is more slow. Chromate of silver, probably on account of its perfect insolubility, is extremely slowly reduced; cadmium is the most effective metal for the purpose. Chloride of silver is rapidly reduced by most of the metals which form soluble chlorides, such as zinc, iron, cadmium, cobalt, and arsenic; lead, nickel, copper, antimony, and mercury, act slowly; and tin and bismuth are very feeble in their action. Zinc, copper, and arsenic, rapidly reduce the ammoniacal solution of oxide of silver. Of all the metallic precipitants zinc and cadmium are the most effective; but when zinc or antimony are used, the separated silver is alloyed with those metals.

## § XXXI. GOLD.

GOLD has been known from the remotest ages; it is the *sol* of the alchemists, and they represented it by the circle  $\odot$ , which is also the emblem of perfection.

Gold occurs in nature in a metallic state, alloyed with a little silver or copper, and in this state it is called *native gold*. Its colour is various shades of yellow; it is either massive, ramose, or crystallized in cubes and octoëdra. The veins of gold are confined to primitive countries, but large quantities of this metal are collected in alluvial soils and in the beds of certain rivers, more especially those of the west coast of Africa, and of Peru, Brazil, and Mexico. In Europe, the streams of Hungary and Transylvania have afforded a respectable quantity of gold; it has been found also in the Rhine, the Rhone, and the Danube. Small quantities have been collected in Cornwall, and in the county of Wicklow in Ireland.

Gold may be obtained pure by dissolving one part by weight of standard gold in three of nitro-muriatic acid, (composed of one part, by weight, of nitric, and two of muriatic acid,) evaporating the solution to dryness, (by a gentle heat towards the end of the process,) redissolving the dry mass in distilled water, filtering, and adding to it a solution of protosulphate of iron; a black powder falls, which, after having been washed with dilute muriatic acid and distilled water, affords, on fusion, a button of pure gold. For the purpose of solution it may conveniently be kept in the pulverulent state.

Gold is of a deep and peculiar yellow-colour. It melts at a bright red-heat, equivalent, according to Daniell, to  $2016^{\circ}$  of Fahrenheit's scale, and when in fusion appears of a brilliant greenish colour. Its specific gravity is 19.3

Gold is so malleable, that it may be extended into leaves which do not exceed one two hundred and eighty two thousandth of an inch in thickness, or a single grain may be extended over 56 cubic inches of surface. It is also so ductile that a grain may be drawn out into 500 feet of wire. It shows no tendency to unite to oxygen when exposed to its action in a state of fusion; but if an electric discharge be passed through a very fine wire of gold, a purple powder is produced, which has been considered as an oxide, though probably it is only finely-divided gold.

There is considerable difficulty in determining the equivalent of gold in consequence of the indefinite character of its protocompounds: hence Gmelin adopts the number 66 as its equivalent; Thomson 100; and Turner 199.2. Following Dr. Turner in the view which he takes of the atomic constitution of the oxides and chlorides of gold, I have assumed 200 as its equivalent, though Thomson's number is most consistent with that deduced from the specific heat. (p. 149.)

PROTOXIDE OF GOLD ( $au + o$ ) may be obtained by the action of potassa on *protochloride* of gold; the product must be washed with water, and dried at a temperature of  $100^{\circ}$ ; if the heat exceed this, a portion of the oxide is reduced, and it is converted into peroxide and metallic gold; it is of an olive-colour. It consists of

					Berzelius.		
Gold . . . . .	1	..	200	..	96.25	..	96.13
Oxygen . . . . .	1	..	8	..	3.75	..	3.87
	1		208		100.00		100.00

DEUTOXIDE OF GOLD. The existence of this step of oxidizement is very doubtful: it is stated to be the product of the combustion of gold by electricity, as when a powerful electric battery is discharged through a fine wire or leaf of gold: in these cases it is dissipated into a purple powder, which has been called the *purple oxide of gold*, but it is probably only the metal in a state of very minute division: at all events, we have no experimental evidence to prove that it is an oxide.

PEROXIDE OF GOLD. According to Pelletier, the best process for obtaining peroxide of gold consists in the decomposition of the *perchloride* by magnesia, washing the precipitate with dilute nitric acid, to remove any excess of the precipitant, and drying it at a very low heat. Dr. Turner, upon the authority of Dr. Wagner of Pesth in Hungary, suggests the following as the most certain process for procuring peroxide of gold. Dissolve one part of gold in the usual way, render it neutral by evaporation, and redissolve in 12 parts of water; to the solution add 1 part of carbonate of potassa, dissolved in twice its weight of water, and digest at about 170°; carbonic acid gradually escapes, and the hydrated peroxide, of a brownish-red colour, subsides; after being well washed, it is dissolved in colourless nitric acid of the specific gravity 1.4, and the solution decomposed by admixture with water; the hydrated peroxide is thus obtained quite pure, and is rendered anhydrous by exposure to a temperature of 212°. In this anhydrous state it is nearly black; insoluble in water, and decomposed either by exposure to solar light or by heat. It is soluble in muriatic acid, forming the common solution of gold; and it dissolves in sulphuric and in nitric acid, but the affinity is here so weak that the solutions are decomposed by the action of water, and yield no saline compound when evaporated with the utmost caution. These properties led Pelletier to examine the action of alkalis upon this oxide, and he found that, digested in a solution of caustic potassa, it was dissolved; it also combines with baryta; and in these cases apparently plays the part of a weak acid; it may, therefore, be called *auric acid*. Boiled with chloride of potassium or sodium, a yellow solution results, which is alkaline, and contains chloride of gold and aurate of potassa or soda. The action of ammonia on chloride of gold will presently be noticed.

This oxide consists of

					Berzelius.		
Gold . . . . .	1	..	200	..	89.5	..	89.23
Oxygen . . . . .	3	..	24	..	10.5	..	10.77
	1		224		100.0		100.00

PROTOCHLORIDE OF GOLD. (*au + c.*) When perchloride of gold is placed on a sand-heat in a porcelain capsule, and exposed, under frequent stirring, to the temperature of melting tin till it no longer evolves chlorine, a white saline mass remains, which, unless it contains undecomposed perchloride, is not soluble in water: it may be preserved unchanged whilst dry, but in contact of water it gradually changes into perchloride

and metallic gold: this decomposition of the protochloride is instantaneous when boiling water is poured upon it, 2 parts of metallic gold being separated for 1 that is held in solution. Protochloride of gold consists of

				Berzelius.
Gold	.	.	1	200
Chlorine	.	.	1	36
			<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
			1	236
				84.74
				15.36
				<hr style="width: 50%; margin: 0 auto;"/>
				100.00
				<hr style="width: 50%; margin: 0 auto;"/>
				85
				15
				<hr style="width: 50%; margin: 0 auto;"/>
				100

**PERCHLORIDE OF GOLD.** ( $Au + 3 Cl$ .) When gold in a state of minute division is heated in chlorine, a compound of a deep-yellow colour results. Gold-leaf also dissolves easily in a strong aqueous solution of chlorine, and affords a similar compound on evaporation. The common solvent of gold, however, for the purpose of obtaining the chloride, is the nitromuriatic acid, composed of two parts of muriatic and one of nitric acid. By evaporation, the saturated solution affords prismatic crystals of a deep orange-colour, very deliquescent, and readily decomposed by heat, yielding at first, the protochloride, and ultimately, pure gold. It is said, that when heated, a very minute portion of the metal also passes off with the chlorine and water. When concentrated sulphuric acid is poured into a strong solution of this compound, it causes a precipitation of *anhydrous chloride of gold*. The colour of its aqueous solution varies; if neutral and concentrated it is nearly red (*Leo ruber* of the alchemists), if dilute, or acid, it is yellow.

The aqueous solution of perchloride of gold, or *muriate of gold*, as it is usually called, is discoloured by steam in the same way, and apparently from the same cause, as nitrate of silver. (See page 805.) It is decomposed by phosphorus and charcoal, and by sulphurous acid; a piece of paper, moistened with it and exposed to light, also becomes purple in consequence of its decomposition. According to Van Mons, it is decomposed by several vegetable acids, and when mixed with binoxalate of potassa, carbonic acid gas is evolved, and the gold gradually separated. When solution of protosulphate of iron is added to chloride of gold, the mixture instantly acquires a dingy green or brown tinge, and appears of a beautiful green if viewed by strong transmitted light: these appearances depend upon the presence of an infinite number of small particles of gold in the metallic state; they soon subside in the form of a brown powder, which may be collected upon a filter, and with a little borax fused into a button. This method of separating gold from its solution is often convenient in analytical operations. According to Dr. Turner, the mutual action of the protosulphate and perchloride is such, that 6 atoms of protosulphate of iron, and 1 of perchloride of gold, produce 2 atoms of persulphate of iron, 1 of perchloride of iron, and 1 of gold. Protochloride of tin, added to a dilute solution of chloride of gold, occasions an instant change of colour to a reddish-brown or dirty-purple: if a piece of tin-foil be immersed in a dilute solution of the chloride, the same purple powder is presently thrown down upon it; it is also formed when an alloy of 150 parts of silver, 35 of tin, and 20 of gold, is digested in nitric acid; nitrate of silver is dissolved, and the purple powder remains. This powder is used in enamel-painting, and for tingeing glass of a fine red colour, under

the name of *purple of Cassius*: it is a compound of peroxide of tin and oxide of gold, the latter metal appearing to be in a very low state of oxidizement, and yet soluble in muriatic acid; it is also soluble in ammonia, forming a deep-purple liquor. It would appear, from Proust's experiments, to consist of about three parts of oxide of tin, and one of protoxide of gold. Oberkampf found the composition and colour of the precipitates formed by protochloride of tin, in solutions of gold, liable to much variation. When the tin predominates, it is of a violet-colour; but when the gold is in excess, it is more pink; and these colours are also communicated to enamel. Oberkampf and Macardieu assert, that the gold in the compound is in the metallic state; that the violet combination contains 60 oxide of tin, and 40 gold; and the pink about 20 and 80. (*Ann. de Chim. et Phys.*, xxx., 147.)

According to Berzelius, the purple of Cassius, when heated to redness, loses between 7 and 8 *per cent.* of water, and the residue is a mixture of metallic gold and peroxide of tin. (See also Gay Lussac, *Ann. de Chim. et Phys.*, xlix.) According to Dr. Turner, the purple of Cassius is a hydrated double salt, composed of peroxide of tin, as the *acid*, united with protoxide of tin, and binoxide of gold, as *bases*, in such proportion that the oxygen of the gold exactly suffices to convert the protoxide into peroxide of tin.

When nitrate or sulphate of silver is added to chloride of gold, a precipitate falls, consisting of chloride of silver and oxide of gold; the latter may be removed by muriatic acid. The protosalts of mercury are rendered deep-brown, or reddish-brown, by chloride of gold, and many organic substances give it a purple tint.

If a solution of chloride of gold be mixed with sulphuric ether, it abstracts the chloride from the water, and an *ethereal solution of chloride of gold* is obtained. Polished steel dipped into this solution, acquires a coat of gold, and it has hence been employed for gilding delicate cutting instruments. It gradually deposits films of metallic gold, sometimes in ramose or arborescent crystals. Perchloride of gold consists of

						Berzelius.
Gold . . . . .	1	..	200	..	65	.. 65.09
Chlorine . . . . .	3	..	108	..	35	.. 34.91
	1		308		100	100.00

**FULMINATING GOLD; AURATE OF AMMONIA; AMMONIURET OF PEROXIDE OF GOLD.** When liquid ammonia is added to a concentrated solution of chloride of gold diluted with about three parts of water, a yellowish-brown precipitate is formed, which, if collected upon a filter, washed with a little water, and carefully dried at the temperature of 212°, is *fulminating gold*. Bergman first showed that this compound consists of about five parts of peroxide of gold and one of ammonia: when heated to about 400°, it explodes violently, the gold is reduced, and nitrogen and water are evolved; hence it appears that the ammonia is decomposed; that its hydrogen, uniting with the oxygen of the oxide, forms water, and that the nitrogen is suddenly liberated. It explodes by friction with hard bodies, and by an electrical shock. If two or three grains be detonated upon a thin piece of platinum-leaf, the metal is torn at the point

of contact, as is the case with all these detonating compounds. This compound probably consists of 2 atoms of ammonia and 1 of peroxide of gold.

**AURO-CHLORIDES.** Under this term are comprehended the compounds described by Bonsdorff (*Ann. de Chim. et Phys.*, xliv.) and others, in which the chloride of gold is combined with certain electro-positive chlorides, such as those of the alkaline bases: they consist of 1 atom of terchloride of gold, and 1 atom of the other chloride, and may be formed of their respective chlorides in such proportions; some of them have been long known; they mostly form prismatic crystals, and include water of crystallization. It is in consequence of the formation of these soluble double salts, that the solution of chloride of gold in muriatic acid yields no precipitates with the alkalis, even when added in excess.

**IODIDE OF GOLD.** The action of *iodine* on gold has been examined by M. Pelletier. (*Quarterly Journal*, x., 121.) When hydriodate of potassa is added to chloride of gold, it produces a very copious yellowish-brown precipitate, insoluble in cold water, and easily decomposed by heat, and by the liquid alkalis. When boiled in water, to deprive it of excess of iodine, it probably consists of

				Pelletier.				
Gold	. . . .	1	..	200	..	61.5	..	66
Iodine	. . . .	1	..	125	..	38.5	..	34
		1		325		100.0		100.

**BROMIDE OF GOLD.** Bromine combines with gold, and forms a dark-gray substance, soluble in water, and crystallizing from its solution in deep-brown crystals. This salt has so intense a colour, that it communicates a tinge to 5000 parts of water. (Balard, *Ann. de Chim. et Phys.*, xxxii., 362.)

**SULPHURET OF GOLD** is procured by passing sulphuretted hydrogen through an aqueous solution of chloride of gold. It falls in the form of a black powder, easily resolved by heat into metallic gold and sulphur. (Oberkampf, *Ann. de Chim.*, lxxx.) It consists of

				Oberkampf.		Bucholz.		
Gold	. . . .	1	..	200	..	80.6	..	82
Sulphur	. . . .	3	..	48	..	19.4	..	18
		1		248		100.0		100.

**PHOSPHURET OF GOLD** is obtained by heating gold-leaf with phosphorus, in a tube deprived of air. It is a gray substance of a metallic lustre, and consists probably of one proportional of gold and one of phosphorus. It is decomposed when heated under exposure to air.

**CYANURET OF GOLD** is thrown down as an insoluble pale-yellow compound, by adding cyanuret of potassium to chloride of gold; it forms, according to Ittner, double salts with the cyanurets of the alkaline bases.

**SULPHOCYANURET OF GOLD** is a flesh-coloured powder, which falls when solution of sulphocyanuret of potassium is mixed with chloride of gold: it is soluble in the precipitant and in ammonia. (Grotthuss.)

**ALLOYS OF GOLD.** An interesting detail of an extended series of experiments upon the *alloys of gold* has been published in the *Phil. Trans.* for 1803, by Mr. Hatchett: his experiments were generally made



with eleven parts of gold and one of alloy; or 38 grains of alloy to the ounce of gold. The alloys of gold with *potassium* and *sodium* have not been examined. With *manganese* it forms a gray brittle alloy. With *iron* the alloy is malleable and ductile, and harder than gold; its colour dull-white, and its specific gravity 16.885. The metals expand by union; so that, supposing their bulk before combination to have been 1000, after combination it is 1014.7. With *zinc* the compound is brittle and brass-coloured: specific gravity 16.937. The metals contract a little in uniting; the original bulk being 1000, that of the alloy is 997. The brittleness continued when the zinc was reduced to  $\frac{1}{10}$  of the alloy. The fumes of zinc in a furnace containing fused gold, make it brittle. *Tin* formed a whitish alloy, brittle when thick, but flexible in thin pieces: specific gravity 17.307: bulk before fusion 1000; after fusion 981; so that there is considerable contraction. The old chemists called tin, *diabolus metallorum*, from its property of rendering gold brittle; but Mr. Bingley's experiments quoted by Mr. Hatchett, show that  $\frac{1}{10}$  of tin does not render gold brittle. The alloy of *lead* is very brittle when that metal only constitutes  $\frac{1}{1520}$  of the alloy; even the fumes of lead destroy the ductility of gold: the specific gravity is 18.080; and 1000 parts become 1005. A very remarkable fact in respect to this alloy is, that its specific gravity diminishes to a certain extent, as the proportion of lead diminishes, and is at its maximum when the lead amounts only to  $\frac{1}{10}$ th part, the quantity of gold remaining the same, and the deficiency being made up with copper. The following table, drawn up by Mr. Hatchett, exhibits this remarkable fact:—

METALS.	Grains.	Sp. Gravity of Alloy.	Bulk before Union.	Bulk after Union.	Expansion.
Gold . .	442	18.080	1000	1005	5
Lead . .	38				
Gold . .	442	17.765	1000	1005	6
Copper . .	19				
Lead . .	19				
Gold . .	442	17.312	1000	1022	22
Copper . .	30				
Lead . .	8				
Gold . .	442	17.032	1000	1035	35
Copper . .	34				
Lead . .	4				
Gold . .	442	16.627	1000	1057	57
Copper . .	37.5				
Lead . .	0.5				
Gold . .	442	17.039	1000	1031	31
Copper . .	37.75				
Lead . .	0.75				

The alloy with *nickel* was of a brass-colour and brittle. The specific gravity of the gold being 19.172, and of the nickel 7.8, that of the alloy

was 17.068. An expansion had taken place, 1000 parts before fusion having become 1007. With *cobalt* the alloy was very brittle: specific gravity 17.112. 1000 parts became 1001 after fusion. With *bismuth* the alloy was of a brass-colour, very brittle, and of a specific gravity = 18.038. 1000 parts became 988 after fusion, so that the condensation was considerable. When the bismuth amounted only to  $\frac{1}{15\frac{1}{2}0}$ th part, the alloy was still brittle, though the colour was nearly that of gold.

With *copper* (*standard gold*) the alloy is perfectly ductile and malleable, but harder than pure gold, and resists wear better than any other alloy, except that with silver. Its specific gravity is 17.157. Gold coin is an alloy of eleven parts of gold and one of copper; of this alloy, 20 troy pounds are coined into 934 sovereigns and one half-sovereign; one pound formerly was coined into  $44\frac{1}{2}$  guineas; it now produces  $46\frac{2}{3}$  sovereigns\*. *Arsenic* and *antimony*, when alloyed in very small proportions with gold, destroy its colour and render it quite brittle.

**ASSAY OF GOLD.** The analysis of most of the alloys of gold is performed by cupellation. The triple alloy of gold, silver, and copper, may be analyzed by digesting it in nitric acid, which takes up the silver and copper, and leaves the gold in the form of a black powder, which may be fused into a button, and weighed. The silver may be thrown down in the state of chloride, by solution of common salt, and the copper precipitated by iron. The *assay of gold* is more complicated than that of silver, in consequence of the double operation which it has to undergo, namely, first, cupellation, and then the separation of the silver by the action of nitric acid. The real quantity of gold or silver taken for an assay is very small; whatever it may be, it is called the *assay pound*. The silver assay pound is divided into 12 ounces, and each ounce into penny-weights and half penny-weights. The gold assay pound is subdivided into 24 carats, and each carat into 4 carat grains, quarters, and eighths. (Aikin's *Dictionary*, Art. ASSAY. See also the authorities above quoted.)

*Mercury* and gold combine with great ease, and produce a white amalgam, much used in gilding. For this purpose the amalgam is applied to the surface of the silver; the mercury is then driven off by

\* All the gold at present coined in our Mint is alloyed with copper only; previous to the year 1826, the alloy consisted in part of silver; hence the paler colour of the sovereigns and half sovereigns of former coinages: an alloy composed of equal parts of silver and copper furnishes the best addition to gold for the purpose of coinage, and it is to be regretted that this requisite portion of silver is not made part of the *value* of the coin, by which, the system of melting down our gold coin for the purpose of extracting its silver would be prevented, and the perfection and facility of coinage ensured. To separate the silver from gold, the alloy is melted with great excess of silver, granulated, and boiled in sulphuric acid (in vessels of platinum), by which the silver is oxidized and converted into sulphate of silver, and the metallic gold remains in the form of an insoluble black powder, which is afterwards collected, washed, and fused into a button or ingot. In the same way, the small quantity of gold contained in silver coin, which used to pass unheeded, is extracted by sulphuric acid; the recently-coined silver, will accordingly be found destitute of those traces of gold which are contained in our coin of a date anterior to 1826, and in Spanish dollars and other foreign silver. Absolutely *pure* copper is essential to the ductility of the above alloys, and much mischief results from its occasional *impurity*.

heat, and the gold remains adhering to the silver, and is burnished. This process is called *water-gilding*. In gilding porcelain, *gold powder* is generally employed, obtained by the decomposition of the chloride; it is applied with a pencil, and burnished after it has been exposed to the heat of the porcelain-furnace. Many curious facts relating to the properties of gold, and its uses in the arts, will be found in Dr. Lewis's *Philosophical Commerce of the Arts*.

CHARACTERS OF THE SALTS OF GOLD. It will be observed from the preceding account, that there are, strictly speaking, no oxysalts of gold, but that it forms haloid combinations, which are easily decomposed and reduced by heat: such of these as are soluble, are recognised by the peculiar precipitates which they afford with protochloride of tin and protosulphate of iron, and by a black precipitate with protonitrate of mercury. Gold is precipitated in the metallic state from its chloride, or muriatic solution, by the greater number of the metals: iron, copper, zinc, and tin, rapidly effect this reduction; lead, mercury, and antimony, more slowly; the tardiness of action is sometimes caused by the adhesion of a film of gold to the precipitating metal. When silver is used, the production of its chloride also impedes the effect: and the same happens with palladium. The gold is generally separated in the form of a brown powder; but copper, iron, zinc, and cadmium, occasion the appearance of a metallic film: and bismuth, antimony, arsenic, and palladium, become coated with a brilliant covering. Tin, after the separation of a part of the gold, forms the purple of Cassius.

### § XXXII. PLATINUM.

THIS metal was first made known in Europe by Mr. Charles Wood, who met with its ore in the West Indies, in 1741, and sent specimens of it to Dr. Brownrigg, which he afterwards presented to the Royal Society. In 1750, a paper was published upon it by Mr. Wood, (*Phil. Trans.*,) and by Dr. Lewis, in 1754. In 1752 a dissertation upon it was published by Scheffer, of Sweden; and in 1757 by Margraaf. (*Mém.*, Berlin.) The labours of later experimentalists in reference to this metal, I shall presently have occasion to quote.

Platinum is found in the metallic state, in small grains, in South America, confined to alluvial strata, chiefly in Brazil and Peru. It has also been found in the province of Antioquia, in North America; and in considerable quantities in the Uralian mountains of Siberia. (*Edin. Quart. Jour. of Science*, v. 323.) The grains, besides platinum, contain generally gold, iron, lead, palladium, rhodium, iridium, and osmium, and often oxide of titanium and chromate of iron. Rounded masses of the metal, however, occasionally occur among them, and are met with in mineral collections; these are rarely larger than a small marble, though some have been found of the size of a pigeon's egg and upwards.

The pure metal\* may be obtained by dissolving crude platinum in nitro-muriatic acid, and precipitating by a solution of muriate of ammonia. The first precipitate is heated, redissolved in nitro-muriatic

\* The method followed in Paris for obtaining pure platinum is described at length by M. Baruel in the 12th volume of the *Quarterly Journal of Science*, O.S.

acid, and again precipitated as before. The second precipitate is heated white-hot, and pure platinum remains. It is a white metal, extremely difficult of fusion, and unaltered by the joint action of heat and air. It varies in density from 21. to 21.5, according to the degree of mechanical compression which it has sustained; it is extremely ductile, but cannot be beaten out into such thin leaves as gold and silver.

The following details respecting the mode of purifying platinum, and rendering it malleable, are taken from Dr. Wollaston's latest paper upon this subject published in the *Philosophical Transactions* for 1829.

“The usual method of giving chemical purity to this metal, by solution in aqua regia and precipitation with sal-ammoniac, are known to every chemist; but I doubt whether sufficient care is usually taken to avoid dissolving the iridium contained in the ore, by due dilution of the solvent. In an account which I gave in the *Philosophical Transactions* for 1804, of a new metal, Rhodium, contained in crude platina, I have mentioned this precaution, but omitted to state to what degree the acids should be diluted. I now, therefore, recommend, that to every measure of the strongest muriatic acid employed, there be added an equal measure of water; and, that the nitric acid used be what is called “single aquafortis;” as well for the sake of obtaining a purer result, as of economy in the purchase of nitric acid. With regard to the proportions in which the acids are to be used, I may say, in round numbers, that muriatic acid, equivalent to 150 marble, together with nitric acid equivalent to 40 marble, will take 100 of crude platinum; but in order to avoid waste, and render the solution purer, there should be in the menstruum a redundance of 20 *per cent.* at least of the ore. The acids should be allowed to digest three or four days, with a heat gradually raised. The solution, being then poured off, should stand until a quantity of fine pulverulent ore of iridium, suspended in the liquid, has subsided; and should then be mixed with 41 parts of sal-ammoniac, dissolved in about five times their weight of water. The first precipitate, which will thus be obtained, will weigh about 165 parts, and will yield about 66 parts of pure platinum. As the mother-liquor, will still contain about 11 parts of platinum, these, with some of the other metals yet held in solution, are to be recovered, by precipitation from the liquor with clean bars of iron, and the precipitate is to be redissolved in a proportionate quantity of aqua-regia, similar in its composition to that above directed: but in this case, before adding sal-ammoniac, about one part by measure of strong muriatic acid should be mixed with 32 parts by measure of the nitro-muriatic solution, to prevent any precipitation of palladium or lead along with the ammonio-muriate of platinum. The yellow precipitate must be well washed, in order to free it from the various impurities which are known to be contained in the complicated ore in question; and must ultimately be well pressed, in order to remove the lost remnant of the washings. It is next to be heated, with the utmost caution, in a black-lead pot, with so low a heat as just to expel the whole of the sal-ammoniac, and to occasion the particles of platinum to cohere as little as possible; for on this depends the ultimate ductility of the product.

“The gray product of the platinum, when turned out of the crucible,

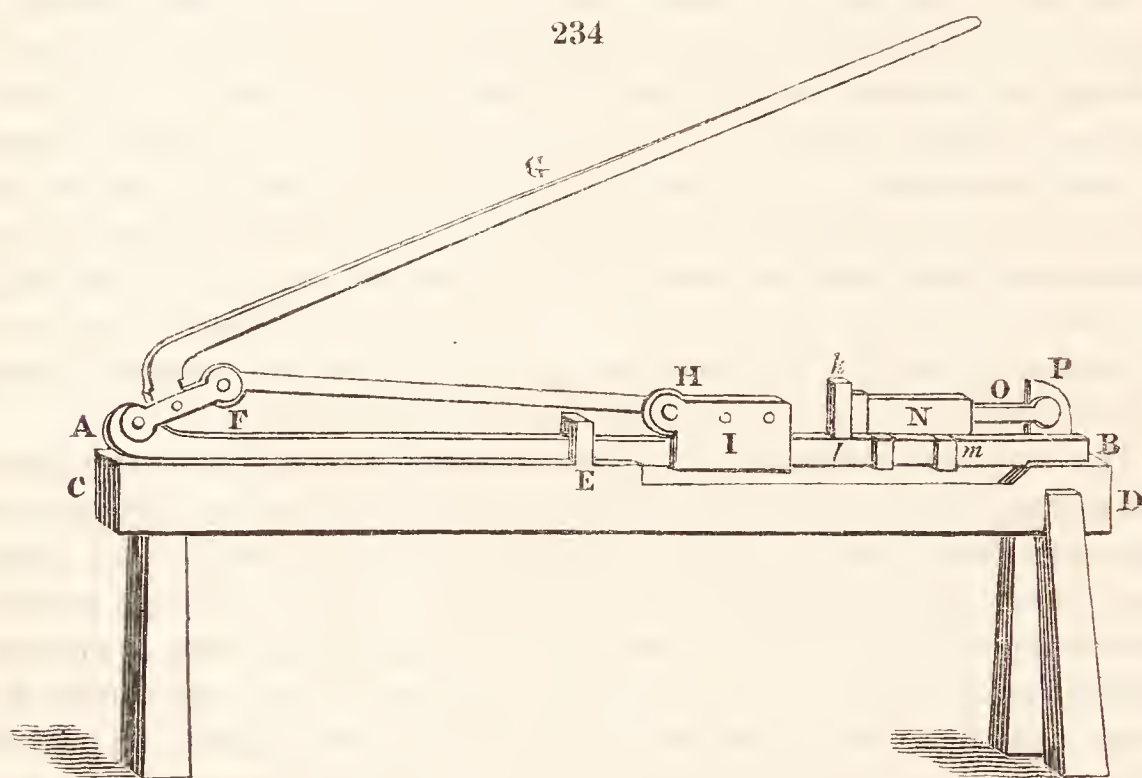
if prepared with due caution, will be found lightly coherent, and must then be rubbed between the hands of the operator, in order to procure, by the gentlest means, as much as can possibly be so obtained, of metallic powder, so fine as to pass through a fine lawn sieve. The coarser parts are then to be ground in a wooden bowl with a wooden pestle, but on no account with any harder material, capable of burnishing the particles of platinum; since every degree of burnishing will prevent the particles from cohering in the further stages of the process. Since the whole will require to be well washed in clean water, the operator, in the later stages of grinding, will find his work facilitated by the addition of water, in order to remove the finer portions, as soon as they are sufficiently reduced to be suspended in it.

“Those who would view this subject scientifically should here consider, that as platinum cannot be fused by the utmost heat of our furnaces, and consequently cannot be freed, like other metals, from its impurities, during igneous fusion, by fluxes, nor be rendered homogeneous by liquefaction, the mechanical diffusion through water should here be made to answer, as far as may be, the purposes of melting; in allowing earthy matters to come to the surface by their superior lightness, and in making the solvent powers of water effect, as far as possible, the purifying powers of borax and other fluxes in removing soluble oxides.

“By repeated washing, shaking, and decanting, the finer parts of the gray powder of platinum may be obtained as pure as other metals are rendered by the various processes of ordinary metallurgy; and, if now poured over, and allowed to subside in a clean basin, a uniform mud or pulp will be obtained, ready for the further process of casting.

“The mould which I have used for casting is a brass barrel,  $6\frac{3}{4}$  inches long, turned rather taper within, with a view to facilitate the extraction of the ingot to be formed, being 1.12 inches in diameter at top, and 1.23 inches at a quarter of an inch from the bottom, and plugged at its larger extremity with a stopper of steel, that enters the barrel to the depth of a quarter of an inch. The inside of the mould being now well greased with a little lard, and the stopper being fitted tight into the barrel by surrounding it with blotting-paper, (for the paper facilitates the extraction of the stopper, and allows the escape of water during compression,) the barrel is to be set upright in a jug of water, and is itself to be filled with that fluid. It is next to be filled quite full with the mud of platinum; which, subsiding to the bottom of the water, is sure to fill the barrel without cavities, and with uniformity,—a uniformity to be rendered perfect by subsequent pressure. In order, however, to guard effectually against cavities, the barrel may be weighed after filling it, and the actual weight of its contents being thus ascertained, may be compared with that weight of platinum and water which it is known by estimate that the barrel ought to contain. A circular piece of soft paper first, and then of woollen cloth, being laid upon the surface, allow the water to pass, during partial compression by the force of the hand with a wooden plug. A circular plate of copper is then placed upon the top, and thus sufficient consistency is given to the contents to allow of the barrel being laid horizontally in a forcible press.

“The press which I have generally used for this purpose consists of a flat iron bar *AB*, set edgewise, and screwed down by a hook *E*, near its middle, where it would otherwise be liable to bend, to a strong wooden bench *CD*. The bar is connected by a pivot at its extremity *A*, with the lever *AFG*. An iron rod *FH*, which turns at its two extremities upon the pivots *F* and *H*, proceeds from the lever at *F*, and, as the lever descends, propels forward the carriage *I*, which slides along the bar. A stopper or block being placed in the vacant space *Ik*, the carriage communicates motion to the cradle *klm*, which is also made to slide along the bar, and carries the barrel *N*, which lies upon the cradle, straight against the piston *O*, which rests by its end against *P*, a projection in the further extremity of the bar.



“The weight, which in this machine, when the angle of the lever’s elevation is small, will keep the power, applied vertically at the extremity of the lever, *in equilibrio* = that power  $\times \frac{AG \times FH}{AF [AF + FH]}$   $\times$  cotan.

of the angle of the lever’s elevation; which expression, in the case of the press actually used, becomes, power  $\times$  5. cotan. of the angle of the lever’s elevation. This expression, at an elevation of  $5^\circ$ , becomes nearly  $60 \times$  power, and at an elevation of  $10^\circ$  becomes nearly  $300 \times$  power; and when the lever becomes horizontal, the multiplier of the power becomes *quasi* infinite. This explanation will be sufficient to show the mechanical advantage with which, by means of this press, the weight of the operator, acting on the end of the lever, will be made to bear against the area of the section of the barrel, a circle little more than an inch in diameter. After compression, which is to be carried to the utmost limit possible, the stopper at the extremity being taken out, the cake of platinum will easily be removed, owing to the conical form of the barrel; and being now so hard and firm that it may be handled without danger of breaking, it is to be placed upon a charcoal fire, and there heated to redness, in order to drive off moisture, burn off grease, and give to it a firmer degree of cohesion. It is next to be heated in a wind-furnace; and for this purpose is to be raised upon an

earthen stand about  $2\frac{1}{2}$  inches above the grate of the furnace, the stand being strown over with a layer of clean quartzose sand, on which the cake is to be placed, standing upright on one of its ends. It is then to be covered with an inverted cylindrical pot, of the most refractory crucible-ware, resting at its open end upon the layer of sand; and care is to be taken that the sides of the pot do not touch the cake. To prevent the blistering of the platinum by heat, which is the usual defect of this metal in its manufactured state, it is essential to expose the cake to the most intense heat that a wind-furnace can be made to receive, more intense than the platina can well be required to bear under any subsequent treatment; so that all impurities may be totally driven off, which any lower temperature might otherwise render volatile. The furnace is to be fed with Staffordshire coke, and the action of the fire is to be continued for about twenty minutes from the time of lighting it, a breathing heat being maintained during the last four or five minutes. The cake is now to be removed from the furnace, and being placed upright upon an anvil, is to be struck, while hot, on the top, with a heavy hammer, so as at one heating effectually to close the metal. If in this process of forging the cylinder should become bent, it should on no account be hammered on the side, by which treatment it would be cracked irremediably; but must be straightened by blows upon the extremities, dexterously directed, so as to reduce to a straight line the parts which project.

“The work of the operator is now so far complete, that the ingot of platinum may be reduced, by the processes of heating and forging, like that of any other metal, to any form that may be required. After forging, the ingot is to be cleaned from the ferruginous scales which its surface is apt to contract in the fire, by smearing over its surface with a moistened mixture of equal parts by measure of crystallized borax and common salt of tartar, which, when in fusion, is a ready solvent of such impurities\*, and then exposing it, upon a platina-tray, under an inverted pot, to the heat of a wind-furnace. The ingot, on being taken out of the furnace, is immediately to be plunged into dilute sulphuric acid, which in the course of a few hours will entirely dissolve the flux adhering to the surface. The ingot may then be flattened into leaf, drawn into wire, or submitted to any of the processes of which the most ductile metals are capable.

“The perfection of the methods above described, for giving to platinum complete malleability, will best be estimated by comparing the metal thus obtained, in respect of its specific gravity, with platinum which has undergone complete fusion; and by comparing it, in respect of its tenacity, with other metals possessing that quality in the greatest perfection. The specific gravity of platinum, drawn into fine wire, from a button which

\* “The chemist will find this flux very serviceable for removing from his crucible or other vessels of platinum those ferruginous scales with which, after long use, and particularly after being strongly heated in a coal or coke fire, they become incrustated. In the analysis of earthy minerals, I have been in the habit of using a similar flux, composed of two parts by weight of crystallized carbonate

of soda, and one of crystallized borax, well ground together. It has the advantage of not acting, like caustic alkali, upon the platinum crucible, and is a powerful solvent of jargon and many other minerals, which yield with difficulty to other fluxes. If the mineral to be operated on requires oxidation, in order to decompose it, a little nitre or nitrate of soda may be added.”

had been completely fused by the late Dr. E. D. Clarke, with an oxy-hydrogen blowpipe, I found to be 21.16. The aggregate specific gravity of the cake of metallic mud, when first introduced into the barrel, exclusively of moisture, is about 4.3; when taken from the press, it is about 10. That of the cake fully contracted, on being taken out of the wind-furnace before forging, is from 17 to 17.7. The mean specific gravity of the platinum, after forging, is about 21.25, although that of some rods, after being drawn, is 21.4: but that of fine platinum-wire, determined by comparing the weight of a given length of it with the weight of an equal length of gold-wire drawn through the same hole, I find to be 21.5, which is the maximum specific gravity that we can well expect to be given to platinum.

“The mean tenacity, determined by the weights required to break them, of two fine platinum-wires, the one of  $\frac{1}{3600}$ , the other of  $\frac{1}{3850}$  of an inch in diameter, reduced to the standard of a wire  $\frac{1}{10}$  of an inch in diameter, I found to be 409 pounds; and the mean tenacity of eleven wires, beginning with  $\frac{1}{4500}$  and ending with  $\frac{1}{25000}$  of an inch, reduced to the former standard, I found to be 589 pounds; the maximum of these eleven cases being 645 pounds, and the minimum 480 pounds. The coarsest and the finest wire which I tried present exceptions, since a wire of  $\frac{1}{150}$  of an inch gave 290 pounds, and a wire of  $\frac{1}{30000}$  of an inch, 190 pounds. If we take 590 pounds, as determined by the eleven consecutive trials, to be the measure of the tenacity of the platinum prepared by the processes above described, and consider that the tenacity of gold-wire, reduced to the same standard, is about 500, and that of iron-wire 600, we shall have full reason to be satisfied with the processes above detailed, by which platinum has been rendered malleable.”

In addition to the properties of this metal, set forth in the preceding abstract, there are other peculiarities belonging to it, upon which some of its valuable applications in the chemical laboratory depend; such, especially, is the action of *spongy platinum* upon gaseous mixtures, and that of *clean* surfaces of the metal, as described and investigated by Faraday. (p. 353.)

The determination of the equivalent of platinum is open to the same difficulties as that of gold. I have adopted 96, which will be found sufficiently consistent with the analytical results which I shall quote. Dr. Turner, upon the authority of Berzelius, assumes 98.8, and L. Gmelin employs the lower equivalent, 48. The number 96 nearly agrees with the deduction from its specific heat (p. 149.)

PLATINUM AND OXYGEN. The affinity of this metal for oxygen, is like that of gold, extremely feeble; it shows no disposition to become an oxide, by exposure to air or oxygen at any temperature; and although a strong electric discharge, when transmitted through a fine platinum-wire, dissipates it into black dust, this, as in the analogous case of gold, is probably finely-divided metal, and not the result of combustion or oxidization. Four definite oxides of platinum are supposed to exist, but of these only two can be satisfactorily identified.

SUBOXIDE OF PLATINUM. ( $2pl + o$ .) When nitrate of mercury is added to a dilute solution of perchloride of platinum, a powder falls, which, when carefully heated, gives off calomel, and leaves a *black oxide*



of platinum, composed, according to Cooper, of 100 platinum, + 4.5 oxygen. (*Journal of Science and the Arts*, vol. iii.) It forms the base of an excellent black enamel.

PROTOXIDE OF PLATINUM. ( $pl + o.$ ) When protochloride of platinum is gently heated in a solution of caustic potassa, a black oxide is formed, part of which is dissolved by the alkali, and part precipitated: it may be thrown down from its alkaline solution by dilute sulphuric acid. Heated in a retort, it is reduced, with the escape of water and oxygen gas. It slowly dissolves in the acids, most of which decompose it and resolve it into peroxide and metal. According to Berzelius, this is the *protoxide* of platinum, and consists of

								Berzelius.
Platinum . . . .	1	..	96	..	92.31	..	92.40	
Oxygen . . . .	1	..	8	..	7.69	..	7.60	
	1		104		100.00		100.00	

SESQUIOXIDE OF PLATINUM. ( $pl + 1\frac{1}{2}o.$ ) When sulphate of platinum is decomposed by ammonia, and the precipitate boiled in weak solution of potassa and cautiously dried, it constitutes *fulminating platinum*: when this is digested in nitric acid a gray powder remains, composed of 100 platinum, 11.86 oxygen. (E. Davy, *Phil. Trans.*, 1820.) When spongy platinum is heated to redness in an open vessel with caustic potassa, and the product, when cold, washed with water, a gray powder is obtained, which is partly dissolved by the alkali: the residue, washed with dilute nitric acid, and afterwards with water, is also said to be *sesquioxide* of platinum, consisting of

								E. Davy.
Platinum . . . .	1	..	96	..	88.8	..	89.5	
Oxygen . . . .	$1\frac{1}{2}$	..	12	..	11.2	..	10.5	
	1		108		100.0		100.0	

PEROXIDE OF PLATINUM. ( $pl + 2o.$ ) When sulphuret of platinum is digested in nitric acid, and carefully evaporated, or when perchloride of platinum is gently heated in sulphuric acid, a dark-brown solution of *persulphate of platinum* is obtained: if this solution be mixed with nitrate of baryta, sulphate of baryta is thrown down, and pernitrate of platinum remains dissolved; this may be in part decomposed by solution of caustic soda, which forms a yellow precipitate, becoming brown when carefully washed and dried, and which is a *hydrated peroxide*. Heated in a retort, it first gives out water and becomes black; at a higher temperature it evolves oxygen, and the metal is reduced: it has a very feeble attraction for the acids, but readily combines with many of the salifiable bases; it dissolves in the caustic and carbonated alkalis, and may be combined with lime, strontia, and baryta, by adding those earths to its acid solution, when it falls in union with them in the form of a yellow powder. (Berzelius.) This oxide consists of

								Berzelius.	Chenevix.
Platinum . . . .	1	..	96	..	85.71	..	85.87	..	87
Oxygen . . . .	2	..	16	..	14.29	..	14.13	..	13
	1		112		100.00		100.00		100.

PROTOCHLORIDE OF PLATINUM. ( $pl + c.$ ) When perchloride of platinum is exposed in a porcelain capsule to a temperature not exceeding

that of melting tin, it is converted into a gray powder, insoluble in water, and not decomposed by sulphuric or nitric acids. It dissolves in boiling muriatic acid, and is decomposed, as above stated, by caustic alkali, which separates protoxide. It is decomposed at a red-heat, and only gives out chlorine, without a trace of water. It is composed of

Platinum . . .	1	..	96	..	72.75	..	73.3	Berzelius.
Chlorine . . .	1	..	36	..	27.25	..	26.7	
	1		132		100.00		100.0	

PERCHLORIDE OF PLATINUM. ( $pl + 2c$ .) When the solution of pure platinum in nitro-muriatic acid is evaporated, it affords a deep-brown liquid, which shoots into prismatic crystals, consisting of hydrated perchloride of platinum and muriatic acid; on further evaporation it yields a brown saline mass, which becomes deeper coloured upon the expulsion of its combined water. It is then a *perchloride of platinum*, yielding a yellow-brown solution in water, and easily soluble in alcohol and in ether. The alcoholic solution is a useful re-agent to detect the presence of potassa: the salt, the base of which is to be ascertained, is dissolved in the smallest possible quantity of water, and mixed with the alcoholic solution of the perchloride: if it be potassa, a triple salt, insoluble in alcohol, is thrown down; if not, the liquid remains clear. (Berzelius.) This perchloride consists of

Platinum . . .	1	..	96	..	57.1
Chlorine . . .	2	..	72	..	42.9
	1		168		100.0

PLATINO-CHLORIDES. Both the chlorides of platinum enter into definite combination with the chlorides of the alkaline bases, and form *platino-protochlorides*, and *platino-perchlorides*. (Bonsdorff, *Poggendorff's Ann.* xiv.)

PLATINO-PROTOCHLORIDE OF POTASSIUM. ( $pl + po + 2c$ .) This salt was obtained by Magnus in the form of red anhydrous four-sided prisms, insoluble in alcohol, by evaporating a solution of protochloride of platinum and chloride of potassium in muriatic acid. It consists of

Platinum	1	..	96	..	46.2	} or {	Protochloride	1	..	132	..	63.5
Potassium	1	..	40	..	19.2		of Platinum	1	..	76	..	36.5
Chlorine	2	..	72	..	34.6		Chloride of	1	..	76	..	36.5
	1		208		100.0		1		208		100.0	

Analogous *platino-protochlorides*, with muriate of ammonia and chloride of sodium, may be obtained.

PLATINO-BICHLORIDE OF AMMONIA (or of muriate of ammonia); AMMONIO-MURIATE OF PLATINUM. ( $pl + 2c$ ) + ( $A + hc'$ .) This is the well-known yellow powder, which falls when solutions of perchloride of platinum and muriate of ammonia are mixed. When it is exposed to heat it loses a little water, and a compound of muriate of ammonia and protochloride of platinum is at first formed; the ammonia is ultimately decomposed, and the platinum remains in the peculiar spongy state above referred to, and possessed of the power of determining the union of hydrogen and certain other inflammable gases with oxygen, as explained

in the section on Hydrogen. (p. 353.) This ammonio-chloride is very sparingly soluble in pure water; rather more so in water acidulated by muriatic acid. If the solution from which it is precipitated contain iridium or palladium, it has a tawny-red colour; these may be removed by boiling in dilute nitric acid and filtering the red solution whilst hot; as it cools it deposits a red crystalline powder, which is generally a triple salt of iridium, and from which the acid may be poured off for use as before. The results of several analyses of this double chloride indicate that it contains between 40 and 45 *per cent.* of platinum, and, therefore, that it is a compound of

Platinum	1	..	96	..	43.2	}	Bichloride of	}	1	..	168	..	75.7
Chlorine	2	..	72	..	32.5	}	Platinum	}					
Ammonia	1	..	17	..	7.6	}	Muriate of	}	1	..	54	..	24.3
Muriatic acid	1	..	37	..	16.7	}	Ammonia	}					
	1		222		100.0				1		222		100.0

PLATINO-BICHLORIDE OF POTASSIUM. ( $pl + 2c$ ) + ( $po + c$ .) This salt is thrown down in the form of a yellow powder when solutions of chloride of potassium, and of bichloride of platinum, are mixed; it is sparingly soluble in water, and is deposited from its boiling solution in small octoëdral crystals: when heated it evolves chlorine, and leaves a mixture of metallic platinum and chloride of potassium. Its difficult solubility renders bichloride of platinum, as already stated, a useful test of the presence of salts of potassa. It consists of

Bichloride of platinum	. .	1	. .	168	. .	68.8
Chloride of potassium	. .	1	. .	76	. .	31.2
		1		244		100.0

PLATINO-BICHLORIDE OF SODIUM. ( $pl + 2c$ ) + ( $so + c$ .) Chloride of sodium occasions no precipitate with bichloride of platinum, but the mixed solutions yield on evaporation prismatic, or tabular crystals, of a deep orange-colour, soluble in water and in alcohol, and which, when heated, lose 19.25 *per cent.* of water of crystallization, and leave the anhydrous double salt: the crystals, therefore, contain

Bichloride of Platinum.	1	. .	168	. .	59.5	
Chloride of sodium	. .	1	. .	60	. .	21.3
Water	. . . . .	6	. .	54	. .	19.2
		1		282		100.0

PLATINO-BICHLORIDE OF BARIUM. When baryta-water is gradually added to a solution of bichloride of platinum, a precipitate falls composed of baryta and peroxide of platinum (*platinate of baryta*.) The solution contains excess of baryta, which falls in the form of carbonate by exposure to air, and afterwards small crystals of the double salt are deposited. This salt may also be formed by mixing the two chlorides in atomic proportions: the crystals are orange-coloured, and in form and appearance resemble those of chromate of lead. They consist of

Bichloride of platinum	. .	1	. .	168	. .	54.3
Chloride of barium	. .	1	. .	105	. .	34.0
Water	. . . . .	4	. .	36	. .	11.7
		1		309		100.0

PLATINO-CHLORIDES OF CALCIUM AND STRONTIUM have been described by Bonsdorff, as also those of magnesium, manganese, iron, zinc, cadmium, copper, nickel, and cobalt: the crystals of the last eight are isomorphous, and consist of 1 atom of the bichloride of platinum, 1 atom of the basic chloride, and 6 atoms of water.

PLATINO-CHLORIDE OF SILVER is thrown down as a yellow basic salt when solutions of bichloride of platinum, and nitrate of silver are mixed, the residuary liquid remains colourless: boiling muriatic acid abstracts the chloride of platinum, and leaves the chloride of silver nearly without colour. (Vauquelin.)

PROTONITRATE OF PLATINUM is obtained by digesting the protoxide in dilute nitric acid: it is of a very deep brown colour, and is decomposed by evaporation, leaving peroxide of platinum.

PERNITRATE OF PLATINUM, formed by dissolving the peroxide in nitric acid, is of a dark-brown colour: when evaporated to dryness, water digested upon the residue, leaves a subsalt. The addition of potassa throws down half the oxide, and afterwards a triple compound of nitric acid, oxide of platinum, and potassa.

PROTOSULPHURET OF PLATINUM. ( $pl + S.$ ) 1. By heating platinum with sulphur in an exhausted glass tube (E. Davy.) 2. By heating ammonio-muriate of platinum with twice its weight of sulphur, to redness, in a covered crucible (Vauquelin.) It is a gray or black powder; specific gravity 6.2; unaltered by air or water; scarcely attacked by the boiling acids, and decomposed when ignited with chlorate of potassa. It consists of

						Vauquelin.	J.Davy.
Platinum . . .	1	..	96	..	85.72	.. 84.5	.. 84
Sulphur . . .	1	..	16	..	14.28	.. 15.5	.. 16
	<u>1</u>		<u>112</u>		<u>100.0</u>	<u>100.0</u>	<u>100</u>

BISULPHURET OF PLATINUM. ( $pl + 2S.$ ) When a solution of perchloride of platinum is mixed with sulphuret of ammonia or potassium a black powder falls, which when dried in vacuo over sulphuric acid, contains, according to Berzelius, no traces of water. When this precipitate is exposed upon paper to dry in the air, the sulphur absorbs oxygen, and becomes sulphuric acid, which chars the paper. When sulphuretted hydrogen is passed through solution of nitromuriate of platinum, the precipitate which falls consists of chloride and sulphuret of platinum. The anhydrous precipitate consists of

						Vauquelin.	Berzelius.
Platinum . . .	1	..	96	..	75	.. 77	.. 75.25
Sulphur . . .	2	..	32	..	25	.. 23	.. 24.75
	<u>1</u>		<u>128</u>		<u>100</u>	<u>100</u>	<u>100.00</u>

PROTOSULPHATE OF PLATINUM is obtained when a solution of protoxide of platinum in caustic potassa is saturated with sulphuric acid, the liquid poured off, and the precipitate dissolved in dilute sulphuric acid: the concentrated solution is opaque and black; diluted with water it becomes red, and appears gradually to pass into persulphate. Vauquelin obtained this salt by digesting protochloride of platinum in sulphuric acid.

The oxide is slowly precipitated from this sulphate by caustic alkali. (Berzelius.)

PERSULPHATE OF PLATINUM is obtained by acidifying the sulphur in the sulphuret by means of nitric acid. It is of a brown colour, and very soluble in water, alcohol, and ether; and with soda, potassa, and ammonia, it forms triple salts. It is a very delicate test of the presence of gelatine, with solutions of which it forms a brown precipitate.

E. Davy found that the precipitate from solution of sulphate of platinum by a slight excess of ammonia, when boiled in potassa, washed and dried, was a *fulminating platinum*; it explodes at about  $420^{\circ}$ , with a loud report, and appears to be a compound of oxide of platinum, ammonia, and water. (*Phil. Trans.* 1817.) He has also described a very singular compound of platinum (*Phil. Trans.* 1820, p. 108,) obtained by mixing equal volumes of strong aqueous solution of the sulphate and of alcohol. The colour of the sulphate slowly disappears, and in some days a black substance subsides, which is washed and dried. It is also formed by boiling the sulphate and alcohol together for a few minutes. This substance is permanent in the air and insoluble in water. It detonates feebly when heated, and is not affected by chlorine, nor by nitric, sulphuric, and phosphoric acids; but it is slowly soluble in muriatic acid. Put into liquid ammonia, it acquires fulminating properties; and plunged into ammoniacal gas it becomes red-hot: the same phenomenon is exhibited by exposing it to the vapour of alcohol, or by placing it upon a piece of paper moistened with that fluid: in these cases the platinum is reduced with the evolution of heat, and the ignition seems to depend upon the slow combustion of the vapour of the alcohol.

PHOSPHURET OF PLATINUM. According to E. Davy, there are two phosphurets. The first, obtained by heating phosphorus with the metal; the second, by heating phosphorus with the ammonio-muriate of platinum. Platinum crucibles are easily injured by the phosphorus evolved during the decomposition of phosphoric salts.

CYANURET OF PLATINUM has not been obtained in a separate state, nor has the precipitate formed by ferrocyanuret of potassium in a strong solution of bichloride of platinum been satisfactorily examined. A double *cyanuret of platinum and potassium* is obtained according to L. Gmelin as follows: spongy platinum is mixed with its weight of ferrocyanuret of potassium and heated to incipient redness, but not higher: the platinum separates a part of the iron from the cyanogen, and when the mass is dissolved in water the platino-cyanuret may be separated by crystallization; the crystals are yellow in one direction, but blue in the direction of their axes: they effloresce and become pale-red in the air, but still retain 12.4 *per cent.* of water, which requires a higher temperature for its separation. This salt is abundantly soluble in hot water, but the greater part crystallizes as the solution cools: the solution gives a scanty white precipitate, with solutions of the oxides of zinc, tin, and mercury; a pale-blue with the protosalts of iron, and a reddish-brown with the persalts of iron; a greenish blue with the salts of copper: and a white curdy precipitate which blackens by exposure to light, with nitrate of silver: it is not precipitated by nitrate of lead. This salt in crystals, consists, according to Gmelin, of

Platinum	1	..	96	..	45.2
Potassium	1	..	40	..	18.4
Cyanogen	2	..	52	..	23.9
Water	8	..	27	..	12.5
	—		—		—
	1		215		100.0

SULPHOCYANURET OF PLATINUM forms according to Grotthuss a bulky flocculent precipitate of a yellow-colour: it is soluble in acids and in solutions of chloride of potassium and sodium, and in muriate of ammonia: alcohol throws it down again from these solutions.

ALLOYS OF PLATINUM. *Zinc, bismuth, tin, and arsenic*, readily combine with platinum, and form *fusible* alloys. It also unites, though less readily, with *copper, lead, and iron*. If a small piece of *tin, zinc, or antimony*, be rolled up in platinum-leaf, and exposed to the jet of a blow-pipe, the two metals combine with such energy, when nearly white-hot, as to produce a kind of explosion. By combining 7 parts of platinum with 16 of *copper* and 1 of *zinc*, Mr. Cooper obtained a mixture much resembling gold. (*Journal of Science and Arts*, vol. iii. p. 119.) Hermbstadt obtained a gold-colour by combining 16 parts of platinum with 7 of *copper*, and 1 of *zinc*.

Iron and steel increase the fusibility of platinum. The alloys of *steel* and platinum have been examined by Stodart and Faraday. They combine in all proportions, but from 1 to 3 *per cent.* of platinum appears best adapted for cutting-instruments. Equal weights of the two metals produce a fine hard and brilliant alloy, of a specific gravity of 9.862; it appears well adapted for mirrors, for it takes a fine polish and does not tarnish. An alloy of 80 platinum and 20 steel has a specific gravity of 15.88. The alloy of *cobalt* and platinum is fusible. With its weight of *nickel*, platinum forms a pale-yellow alloy, susceptible of a high polish, and obedient to the magnet. *Mercury* does not easily act upon manufactured platinum, but it combines with it in the state of very fine division, in which it is obtained by heating the ammonio-muriate of platinum, and forms a buttery amalgam, which gradually hardens. When fused with *silver* in the proportion of 7 *per cent.* and upwards, it impairs the malleability and colour of the latter metal. This alloy is soluble in nitric acid; so that, if an alloy of *gold* and platinum be fused with silver, rolled into a plate, and digested in nitric acid, both the silver and platinum are dissolved.

Platinum has the property of being united by *welding*, either one piece to another, or with iron, or steel. Wires of steel and platinum, when welded and polished, exhibit a curious and beautiful surface, especially when the steel parts are slightly acted upon by dilute acid. This welding property of platinum may be usefully applied in the arts; wires may be joined so as to form rings and chains; and with a view to economy, platinum may be joined to iron or steel for many uses in the laboratory of the chemist.

The perfection with which vessels of platinum resist the action of heat and air, of most of the acids, and of sulphur and mercury, render them peculiarly valuable in many of their applications: but its high value is against its very general adoption, for, although much cheaper than gold, it is worth between four and five times its weight of silver. Berzelius

observes (Lehrbuch), that in the employment of platinum vessels, the following precautions must be attended to: 1. They must not be subjected to the action of compounds which evolve chlorine. 2. Nitre, and the alkalis, must not be fused in them. 3. No metallic reductions must be performed in them; nor compounds of phosphorus decomposed so as to evolve that substance. 4. When metallic oxides are heated in a platinum crucible, the heat must not be raised beyond redness, provided the oxide is easily decomposed: hence the caution requisite with the oxides of lead, bismuth, copper, cobalt, nickel, and antimony, which, though they may not effect the fusion of the crucible, spoil it by their action upon its interior surface, which is rendered rough and porous. 5. That the immediate contact of the fuel (charcoal should always be used) with the crucible should be avoided as much as possible, especially at very high temperatures; for it is thus, in the process of time, rendered brittle and unsound. Small holes and fissures may be filled up and soldered with pure gold, but in that case the vessel must not be exposed to a white heat, because then the gold and platinum combine.

It would appear from Mr. Daniell's experiments (on a new register pyrometer, *Phil. Trans.*, 1831, p. 315,) that one cause at least of the brittleness which platinum acquires when repeatedly heated in the usual fuel, depends upon the absorption of silicium or silica, to the amount of about 3 *per cent.* A high temperature appears, however, necessary to effect this combination, which is somewhat analogous to the absorption of carbon by iron in the process of making steel by cementation.

CHARACTERS OF THE SALTS OF PLATINUM. The difficult solubility of the ammonio and potasso-chlorides of platinum, and the solubility of the corresponding soda-compounds, are very characteristic of this metal. Phosphate of soda produces no precipitate in chloride of platinum; the ferrocyanurets of potassium throw down the platino-chloride of potassium: cyanuret of mercury occasions no precipitate: iodide of potassium communicates a reddish-brown colour to solutions of the chlorides of platinum, and gradually produces a brown precipitate: and if the mixture be heated in a matrass, the glass acquires a coating of metallic platinum. All the metals which reduce the chloride of gold, with the exception of palladium, act similarly upon chloride of platinum, but its complete separation in the metallic state is slow: iron, zinc, cadmium, and copper, are its most effective precipitants; they separate it as a black powder, which sometimes adheres in films to the glass.

### § XXXIII. PALLADIUM.

PALLADIUM is most easily obtained by the following process. (Wollaston, *Phil. Trans.*, 1805.) Digest the *ore* of platinum in nitro-muriatic acid, neutralize the redundant acid by soda, throw down the platinum by muriate of ammonia, and filter. To the filtered liquor add a solution of cyanuret of mercury; a yellow flocculent precipitate of *cyanuret of palladium* is soon deposited, which yields palladium on exposure to heat.

To obtain malleable palladium, Dr. Wollaston gives the following more explicit directions. (*Phil. Trans.* for 1819.) "The residuum obtained from burning the cyanuret of palladium is to be combined

with sulphur, and each cake of the sulphuret, after being fused, is to be finally purified by cupellation, in an open crucible, with borax and a little nitre. The sulphuret is then to be roasted, at a low red-heat, on a flat brick, and pressed, when reduced to a pasty consistence, into a square or oblong and perfectly flat cake. It is again to be roasted very patiently, at a low red-heat, until it becomes spongy on the surface. During this process sulphur flies off in the state of sulphurous acid, especially at those moments when the heat is allowed occasionally to subside. The ingot is then to be cooled; and when quite cold, is to be tapped with a light hammer, in order to condense and beat down the spongy excrescences on its surface. The alternate roastings and tappings (or gentle hammerings) require the utmost patience and perseverance, before the cake can be brought to bear hard blows; but it may, by these means, at length be made so flat and square, as to bear being passed through the flattening-mill, and so laminated to any required degree of thinness. Thus prepared, it is always brittle while hot, possibly from its still containing a small remnant of sulphur. I have also fused some palladium *per se*, without using sulphur; but I have always found it, when treated in this way, so hard and difficult to manage, that I greatly prefer the former process."

Palladium is of a dull-white colour, malleable and ductile. Its specific gravity is about 11.3. It is hard. It fuses at a temperature above that required for the fusion of gold, and when intensely heated by the oxy-hydrogen blowpipe, it is dissipated in sparks. When heated over the flame of a spirit-lamp, it acquires various shades of blue upon its surface, in consequence of superficial oxidation. The equivalent of palladium appears to be somewhere between 52 and 57. I have adopted 54. (53.3 Turner, 56 Gmelin.)

Dr. Wollaston has ascertained the existence of *native palladium* in the ore of platinum. It is in small fibrous grains.

PROTOXIDE OF PALLADIUM. (*pal* + *o*.) By carefully heating the nitrate of palladium to dull redness, a black oxide is obtained, which dissolves in muriatic acid without evolving chlorine. When nitrate of palladium is precipitated by a caustic alkali, the red, or dark orange-coloured powder which falls, is an *hydrated oxide*. This oxide consists of

						Berzelius.		
Palladium	. . . .	1	..	54	..	87	..	87.56
Oxygen	. . . .	1	..	8	..	13	..	12.44
		1		62		100		100.00

BINOXIDE OF PALLADIUM. (*pal* + 2 *o*.) To prepare this oxide, Berzelius recommends that a solution of potassa, or its carbonate, in excess, should be poured by little and little on the solid bichloride of palladium and potassium, and the materials well intermixed; water is not first added because it decomposes the double chloride, and the alkali is not added all at once, because the oxide would then be dissolved at first, and afterwards separate as a gelatinous hydrate, which could not be purified by washing. When prepared according to the foregoing directions, the binoxide is obtained as a hydrate, of a deep yellowish-brown colour, which retains a little potassa in combination, but on heating the solution to 212° the alkali is dissolved, and the anhydrous black oxide left. (Turner's *Elements*.)



**CHLORIDES OF PALLADIUM.** When the nitro-muriate of palladium is evaporated to dryness, the residue may be heated till it fuses; a black *protochloride* remains, which, at a red-heat, gives out chlorine, and is reduced. A *bichloride* is said to be formed by dissolving the protochloride in nitro-muriatic acid; but it has only been obtained in combination with chloride of potassium, forming a red crystallizable salt—the *palladio-perchloride of potassium*: a similar salt may be formed with muriate of ammonia, which is less soluble, and of a dark-red colour. The *palladio-protochloride of potassium* forms prismatic crystals of a dingy-yellow colour. (Bonsdorff, *Ann. de Chim. et Phys.*, xlv.)

**SULPHURET OF PALLADIUM.** (*pal* + *S*.) This compound is readily formed by fusing sulphur with palladium; it is white, hard, and fusible, and when long exposed to heat and air loses the whole of its sulphur. It is thrown down in the form of a black powder, by the action of sulphuretted hydrogen upon the salts of palladium. It consists of

				Berzelius.		Vauquelin.	
Palladium	. . . 1	. . . 54	. . . 77.2	. . . 78	. . . 80.6		
Sulphur	. . . 1	. . . 16	. . . 22.8	. . . 22	. . . 19.4		
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>		
	1	70	100.0	100	100.0		

**PHOSPHURET OF PALLADIUM** is an easily-fusible compound.

**CARBURET OF PALLADIUM.** Palladium acquires extreme brittleness when long fused in contact with charcoal. When a plate of palladium is held in the flame of alcohol, it becomes covered with carbon, and carbonaceous excrescences gradually form upon it, which, when burned, leave palladium, and the surface of the metal becomes corroded, and its whole substance brittle. When spongy palladium, in the state in which it is obtained by the ignition of its ammonio-chloride, is heated to redness, and placed upon the wick of a spirit lamp, it glows and becomes enveloped in an accumulation of a compound of carbon and palladium. This property of precipitating charcoal from flame, and combining with it, is peculiar to palladium. Platinum and iron show indications of it. (Wöhler, *Poggendorff*, iii., 71.)

**CYANURET OF PALLADIUM.** This compound is formed when a solution of cyanuret of mercury is added to a solution of palladium: it falls in olive-coloured or dingy-yellow flakes: this furnishes a ready method of separating palladium from other metals which are incapable of decomposing the cyanuret of mercury. The cyanuret of palladium, when sufficiently heated, leaves the metal: it dissolves in cyanuret of potassium, and, on evaporation, prismatic crystals of *palladio-cyanuret of potassium* are obtained.

**ALLOYS OF PALLADIUM.** These have not been minutely examined. Like platinum, it destroys the colour of gold; one part, fused with six of gold, forming a white alloy. This compound, from its hardness and durability, was employed, at the suggestion of Dr. Wollaston, for the graduated part of the mural circle, constructed by Mr. Troughton for the Royal Observatory at Greenwich. It readily amalgamates with mercury. Palladium exists in large quantities in some part of South America, for bars of it, weighing several pounds, have been imported from that country, and nearly pure.

CHARACTERS OF THE SALTS OF PALLADIUM. Most of these have been but imperfectly examined. Muriatic acid boiled upon palladium acquires a red-colour. Sulphuric acid becomes blue. Nitric acid readily dissolves it; but its best solvent is nitro-muriatic acid, which forms a fine red solution. The fixed alkalis throw down red or orange-coloured precipitates from these solutions, sparingly soluble in excess of the alkali. Ferrocyanuret of potassium gives an olive-green precipitate; and sulphuretted hydrogen one of a dark-brown colour. Protochloride of tin occasions a brown precipitate in the neutralized solutions of palladium; when dilute, the mixture becomes green. Protosulphate of iron throws down metallic palladium. Many of the other metals precipitate palladium in the metallic state.

### § XXXIV. RHODIUM.

THIS metal, discovered in 1803, by Wollaston, may be obtained as follows:—Digest the *ore* of platinum in nitro-muriatic acid, filter the saturated solution, and pour it into a solution of sal-ammoniac, by which the greater proportion of the platinum is precipitated; filter, and separate the palladium by cyanuret of mercury; filter again, and immerse a plate of zinc into the clear solution, which will become coated with a black powder. Separate this, and digest it in dilute nitric acid, by which a little copper and lead are taken up. Then wash, and digest in dilute nitro-muriatic acid, to which add some common salt; evaporate to dryness, and wash the dry mass repeatedly with alcohol. A deep-red substance remains, which, when dissolved in water, furnishes a black precipitate upon the immersion of a plate of zinc. This, strongly heated with borax, assumes a white metallic lustre, and is rhodium.

Rhodium is very difficult of fusion: its specific gravity is about 11. When pure, the acids do not dissolve it, but they act upon and dissolve several of its alloys, a circumstance which explains its presence in the nitro-muriatic solution of platinum. When an alloy of lead and rhodium is digested in nitro-muriatic acid, it is also readily dissolved, and by evaporation a red compound is obtained, from which chloride of rhodium may be separated by water. The *rose-colour* of this compound suggested the name which has been applied to the metal. Berzelius has shown that metallic rhodium may be oxidized by ignition either with nitre or with bisulphate of potassa, and that when heated with the latter, a double sulphate of peroxide of rhodium and potassa is produced, which yields a yellow solution with hot water: in this way rhodium may be separated from platinum, iridium, and osmium. There is great discrepancy in the equivalent of rhodium given by different chemists; according to the latest experiments of Berzelius, the number 52 has been adopted. (52.2 Turner, 54 Thomson, 120 Gmelin, 45 deduced from earlier experiments.)

PEROXIDE OF RHODIUM. When a mixture of finely-divided rhodium, potassa, and a little nitre, is heated to redness in a silver crucible, and the product washed with water, and then digested in muriatic acid, a hydrated peroxide of rhodium, insoluble in the acid, remains. When heated it becomes black, and probably is then the *protoxide*.

The peroxide is stated to consist of

Rhodium . . .	1	..	52	..	81
Oxygen . . .	1	..	12	..	19
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		64		100

PERCHLORIDE OF RHODIUM was obtained by adding silicated fluoric acid to a solution of rhodio-chloride of potassium, as long as the double fluoride of potassium and silicium was generated, after which the filtered liquid was evaporated to dryness, and [the residue] redissolved in water. This perchloride when dry has a dark-brown colour, is uncrystalline, and decomposed by a full red-heat into chlorine and metallic rhodium. It deliquesces in the air into a brown liquid, and its aqueous solution has a fine red colour, whence the name *rhodium* (from  $\rho\acute{o}\delta\omicron\nu$ , a rose) is derived. (*Ann. de Chim. et Phys.*, xl., 51. Turner's *Elements*, 653.)

This perchloride is represented as consisting of

Rhodium . . .	1	..	52	..	49
Chlorine . . .	$1\frac{1}{2}$	..	54	..	51
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	1		106		100

In combination with the chlorides of potassium and sodium, this perchloride forms double salts. (*rhodio-chlorides*.) They are composed of 1 atom of the perchloride and 1 of the basic chloride.

SULPHURET OF RHODIUM is obtained by heating the metal in a state of fine division with sulphur; or by heating the triple muriate of ammonia and rhodium with sulphur: it is also precipitated by heating the solution of the latter salt with one of an alkaline hydrosulphuret. By the action of nitric acid it is converted into *sulphate of rhodium*.

ALLOYS OF RHODIUM. Rhodium forms malleable *alloys* with the malleable metals, several of which have been examined by Dr. Wollaston. (*Phil. Trans.*, 1804.) It has not been combined with mercury.

With *steel*, rhodium forms an alloy, which probably would be very useful in the arts, were it not for the scarcity of the latter metal. 1 to 2 *per cent.* of rhodium gives steel great hardness, and yet there is sufficient tenacity to prevent cracking either in forging or hammering. (*Quarterly Journal*, ix., 328.) The extreme hardness and durability of rhodium induced Dr. Wollaston to suggest it for the nibs of metallic pens, a purpose to which it has been successfully applied.

CHARACTERS OF THE SALTS OF RHODIUM. These have as yet been but imperfectly examined. Those containing the peroxide are mostly of a red or orange colour; they are precipitated by cyanuret of mercury, by ferrocyanuret of potassium, and by muriate of ammonia. The action of the pure alkalis upon them is very indefinite. According to Pfaff (*Handbuch der Analyt. Chemie*) the salts of the peroxide of rhodium yield a yellow flocculent precipitate, insoluble in excess of the precipitant, to the caustic alkalis: they are not precipitated by carbonated alkalis, nor by solution of muriate of ammonia, if there be excess of acid present: but the perchloride of rhodium yields a difficultly-soluble dingy-yellow precipitate, with excess of ammonia; muriatic acid redissolves it, and forms a red solution.

## § XXXV. OSMIUM.

OSMIUM and Iridium are contained in the black powder which remains after the action of nitromuriatic acid upon the ore of platinum. This residue, when fused with potassa and washed, furnishes a yellow alkaline solution of oxide of osmium. Saturate the alkali with sulphuric acid, pour the mixture into a retort, and distil. A colourless solution of the *oxide of osmium* passes into the receiver, from which almost all the other metals throw down metallic osmium\*.

To obtain the oxide of osmium in a pure, solid, and crystallized state, grind together, and introduce, when ground, into a cold crucible, three parts by weight of the insoluble powder, and one part of nitre. The crucible is to be heated to a good red in an open fire, until the ingredients are reduced to a pasty state, when osmic fumes will be found to arise from it. The soluble parts of the mixture are then to be dissolved in the smallest quantity of water necessary for the purpose, and the liquor thus obtained is to be mixed in a retort, with so much sulphuric acid, diluted with its weight of water, as is equivalent to the potassa contained in the nitre employed: but no inconvenience will result from using an excess of sulphuric acid. By distilling rapidly into a clean receiver, for so long a time as the osmic fumes continue to come over, the oxide will be collected in the form of a white crust on the sides of the receiver, and there melting, it will run down in drops beneath the watery solution, forming a fluid flattened globule at the bottom. When the receiver has become quite cold, the oxide will become solid and crystalline. One such operation has yielded 30 grains of the crystallized oxide, besides a strong aqueous solution of it. This may be agitated with mercury, and the product washed with muriatic acid to remove the oxide of mercury which is formed. The osmium remains in the form of a black powder, which acquires a metallic lustre by friction. In its densest state, its sp. gr., according to Berzelius, is 10. (*Ann. de Chim. et Phys.*, xl. and xlii.) When heated in the air it burns into an oxide, and in its pulverulent state it is attacked by nitric acid; but after exposure to a red-heat in close vessels, it becomes much less oxidable. The equivalent of osmium appears on the authority of Berzelius to be about 100, (99.7 Turner,) and he conceives it susceptible of five degrees of oxidizement.

PROTOXIDE OF OSMIUM ( $OS + O$ ) is obtained by the action of pure alkalis on the protochloride of osmium, or upon the osmio-chloride of potassium; it gradually falls in the form of a nearly black *hydrate*, obstinately retaining a portion of alkali; it dissolves slowly in the acids, forming deep-green or greenish-brown solutions. When heated in a close vessel it gives off water, but does not sublime. It detonates when heated with combustibles. Its equivalent is 108.

SESQUIOXIDE OF OSMIUM ( $OS + 1\frac{1}{2}O$ ) has not been obtained in an insulated state, but is produced in combination with ammonia, when the

\* In reference to the history of osmium, see Mr. Tennant's paper "On two metals found in the powder remaining after the solution of platinum." *Phil. Trans.* 1804; and Dr. Wollaston's paper in the *Phil. Trans.* for 1829.

binoxide is heated with excess of ammonia, nitrogen being at the same time evolved.

**BINOXIDE OF OSMIUM.** ( $OS + 2O$ .) When a saturated solution of bichloride of osmium, or of the osmio-bichloride of potassium, is heated with carbonate of soda, the binoxide gradually falls; it retains a little alkali, which may be removed by dilute muriatic acid; if it then be washed and dried at  $212^{\circ}$ , it only retains water, which it gives off when heated, and remains anhydrous. In this state it appears insoluble in the acids. Its equivalent is 116.

**TEROXIDE OF OSMIUM** ( $OS + 3O$ ) is prepared as the preceding, from the *terchloride*.

**PEROXIDE OF OSMIUM.** ( $OS + 4O$ .) This is the volatile oxide above adverted to, and is obtained by the combustion of the metal in oxygen, or by the action of boiling nitric acid, or by the fusion of osmium with nitre or with potassa. When osmium is heated, and a current of oxygen passed over it, white or yellowish crystals of the anhydrous peroxide are formed: these dissolve slowly in water, and readily in alcohol and ether; these solutions gradually deposit metallic osmium. Other combustibles deoxidize it; by sulphurous acid its solution is rendered yellow, orange, brown, green, and lastly blue, colours corresponding to the different degrees of oxidizement. It stains the skin. It may be volatilized in hydrogen gas, but when its vapour and hydrogen are passed through a red-hot tube, it is reduced. It is reduced by sulphuretted hydrogen, and sulphuret of osmium is formed. The odour of the vapour of this oxide is very peculiar; it has been by some compared to that of chlorine; it is acrid, and poisonous; when much diluted, it a little resembles the smell of new wheaten bread; this is the origin of the term *osmium*, from  $\delta\sigma\mu\tilde{\eta}$ , *odor*. It has no acid reaction, but as it combines with alkalis, and forms compounds which are permanent at high temperatures, it has sometimes been termed *osmic acid*. When infusion of galls is dropped into its aqueous solution, a very characteristic blue colour is produced, which Berzelius ascribes to a mixture of the peroxide and sesquioxide. The equivalent of this oxide is  $100 + 32 = 132$ .

**CHLORIDES OF OSMIUM.** Berzelius has described four chlorides of this metal, corresponding in composition to the oxides. When chlorine is transmitted over heated osmium, a beautiful dark-green sublimate of *proto-chloride of osmium* is the result. This is succeeded by a red sublimate, which is the *bichloride*. The *sesquichloride* and *perchloride* have not been obtained in a separate state, but Berzelius infers their existence in combination with muriate of ammonia, in certain *osmio-chlorides* of that muriate: he has also examined the double salts, produced by the union of the protochloride and perchloride of osmium with the chloride of potassium.

**SULPHURETS OF OSMIUM.** Sulphur and osmium apparently combine, in several proportions, for sulphuretted hydrogen precipitates it from all its solutions.

The remaining compounds of this remarkable metal have not been sufficiently examined, to enable us to give satisfactory details respecting them. A few of its *alloys* have been noticed by Mr. Tennant, and the characters of its salts will be sufficiently obvious from the preceding statements.

## § XXXVI. IRIDIUM.

THIS metal was discovered by Tennant in 1803, and about the same time by Descotils: the various colours exhibited by the muriatic solution of its oxide suggested its name (from *Iris*, the rainbow). The black powder which remains after native platinum has been digested in nitro-muriatic acid, consists chiefly of iridium and osmium; titanium and chromate of iron also occur in it. To obtain iridium, this powder is fused in a silver crucible, with twice its weight of hydrate of potassa, for the space of an hour or more; the residue is washed, by which, as already stated, the oxide of osmium is removed, and the remaining insoluble portion is *iridium*, which has been oxidized by the process of fusion. This oxide is soluble in muriatic acid, and the solution is blue, if free from iron, which communicates more or less of a green tint: when heated with the addition of a little nitric acid, it becomes red, probably in consequence of the peroxidizement of the iridium. When the muriatic solution of iridium is evaporated, it furnishes brown crystals, which are decomposed by a red-heat, and leave finely-divided metallic iridium. They form a reddish-brown solution with water, which, if concentrated and mixed with a saturated solution of muriate of ammonia, afford a dark-brown precipitate of the *ammonio-muriate of iridium*. The solution of the chloride is decomposed by all the metals except gold and platinum, and metallic iridium precipitated.

Iridium, obtained by immersing a plate of zinc into a solution of the chloride, or by violently heating that salt, is of a whitish colour, and, according to Mr. Children, who succeeded in fusing it by means of his large Voltaic apparatus, its specific gravity is above 18. Its most marked character is extremely difficult solubility in the acids: indeed, when pure, it is probably insoluble, although, when alloyed with platinum, a little is taken up by nitro-muriatic acid. Its equivalent, deduced from the experiments of Berzelius, is the same as that of platinum, namely 96.

**OXIDES OF IRIDIUM.** According to Berzelius there are four oxides of iridium, separable from the corresponding *chlorides* by the action of alkalis. The blue oxide, or that which forms blue solutions with the acids, he considers as a compound of the protoxide and sesquioxide.

**CHLORIDES OF IRIDIUM.** When iridium, heated nearly red-hot, is exposed to a current of chlorine, an olive-coloured *protochloride* is formed, which, at a temperature a little exceeding that required for its production, is reduced. The same compound is obtained in solution, when the hydrated protoxide is dissolved in muriatic acid. A *sesquichloride* is obtained by fusing iridium with nitre, digesting the product in nitric acid, washing the remaining oxide, and dissolving it in muriatic acid; it furnishes a dark-brown solution, which, on evaporation, leaves a brown deliquescent and uncrystallizable residue. The *bichloride* is produced by digesting the sesquichloride in nitro-muriatic acid: its solution is brown, and, when evaporated at a temperature above  $212^{\circ}$ , it loses chlorine and passes into sesquichloride. The *perchloride* has only been obtained in combination with chloride of potassium: it is red when in solution. These chlorides act as haloid acids, and form *iridio-chlorides* with the basic chlorides.

SULPHURETS OF IRIIDIUM. From the colour of the precipitates occasioned by sulphuretted hydrogen in the solutions of the preceding chlorides, it has been inferred that there are four corresponding sulphurets; but these and the other compounds of iridium are too imperfectly known to require further notice.

### § XXXVII. GLUCINUM.

GLUCINUM; GLYCIUM; or BERILLIUM; was first obtained in 1828, by Wöhler, by the action of potassium on *chloride of glucinum*. (See Aluminum.) It is a gray substance, having a slight metallic lustre, and very difficult of fusion. At common temperatures it is not acted on by air or water, but when heated in the air it burns into glucina: it burns vividly in oxygen gas, in chlorine, and in the vapour of iodine and bromine. It combines, with the evolution of heat and light, with sulphur, phosphorus, selenium, and arsenic. (Wöhler, *Ann. de Chim., et Phys.*, 1828.) Its equivalent is doubtful: that deduced from the experiments of Berzelius is about 18. (17.7, Turner and Gmelin.)

OXIDE OF GLUCINUM, or GLUCINA, was discovered in 1798 by Vauquelin, in the *beryl*: it also exists in the *emerald* of Peru, and in *Euclase*. It is white, insipid, and insoluble in water. It has no action on vegetable colours; its specific gravity = 2.97. It dissolves in caustic potassa and soda, but not in ammonia, and thus resembles alumina, but differs from yttria. Again it differs from alumina, but resembles yttria, in being soluble in carbonate of ammonia; it is much more soluble in this solution than yttria. With the acids it forms saline compounds of a sweetish astringent taste, (hence the name; from *γλυκυσ*, *sweet*.) It is not precipitated by ferrocyanuret of potassium.

i. The *beryl* is found in primitive rocks in many parts of the world, but especially fine in Siberia. It is usually transparent, and pale-green or blue. It crystallizes in six-sided prisms.

ii. The *emerald* is principally found in Peru, crystallized in regular six-sided prisms, the edges or angles of which are sometimes replaced by facets. Its colour is green, and it is either transparent or translucent.

iii. *Euclase* is a very rare crystallized mineral, originally found in Peru, but has since been brought in insulated crystals, from the Brazils. These minerals are composed as follows: (Vauquelin; *Journal des Mines*, Nos. 36 and 43.)

	Beryl.		Emerald.		Euclase.
Silica . . . . .	68	..	64.5	..	44.33
Alumina . . . . .	15	..	16.0	..	31.83
Glucina . . . . .	14	..	13.0	..	23.84
Oxide of chromium	—	..	3.0	..	—
Oxide of iron . . .	1	..	—	..	—
Lime . . . . .	2	..	1.5	..	—
Water and loss . .	—	..	2.0	..	—
	<hr/>		<hr/>		<hr/>
	100		100		100.00

To obtain glucina from either of these minerals, proceed as follows: Reduce it to a fine powder, and fuse it with thrice its weight of pure, or carbonate of potassa; dissolve the fused mass in dilute muriatic acid,

and evaporate to dryness; by which the silica is rendered insoluble: digest this dry residue in water acidulated by muriatic acid, and add ammonia, which throws down a mixture of glucina and alumina; wash the precipitate, and digest it whilst moist in excess of carbonate of ammonia, by which the glucina is dissolved, and, on filtering, the alumina remains behind: then boil the filtered liquid, and carbonate of glucina is thrown down, which washed, dried, and heated to redness, affords pure glucina. It consists of

						Berzelius.
Glucinum	1	..	18	..	69	68.83
Oxygen .	1	..	8	..	31	31.17
	1		26		100	100.00

CHLORIDE OF GLUCINUM is obtained by dissolving glucina in muriatic acid, and carefully evaporating to dryness. FLUORIDE OF GLUCINUM is formed in the same manner: after perfect evaporation to dryness of a solution of glucina in hydrofluoric acid, the residue is soluble in water.

NITRATE OF GLUCINA is difficultly crystallizable, deliquescent, and soluble in alcohol.

SULPHATE OF GLUCINA. When glucina is dissolved in excess of sulphuric acid, evaporated till acid begins to escape, and then alcohol added, a crystallizable *bisulphate of glucina* separates, the solution of which dissolves carbonate of glucina, and becomes a *subsulphate*, which is not crystallizable, but which, after evaporation to dryness, is separated by the affusion of water into a *neutral sulphate*, and an insoluble salt containing great excess of base.

PHOSPHATE OF GLUCINA is precipitated in a gelatinous form when phosphate of soda is added to solution of chloride of glucinum.

CARBONATE OF GLUCINA falls in the form of a bulky flocculent precipitate, which is light and soft when dried.

CHARACTERS OF THE SALTS OF GLUCINA. These salts are astringent and sweet: they are precipitated by the caustic fixed alkalis, and the precipitate is re-dissolved by their excess, and sparingly by their carbonates: they are not precipitated by ferrocyanuret of potassium. A characteristic property of glucina is, that when a warm solution is mixed with a warm solution of fluoride of potassium till a precipitate begins to appear, and the mixture then suffered to cool, a difficultly-soluble double salt separates in the form of lamellar crystals. (Berzelius.)

### § XXXVIII. ZIRCONIUM.

SIR H. DAVY first demonstrated the nature of *Zirconia*, and its metallic base was obtained by Berzelius in 1824 by acting upon the potassio-fluoride of zirconium by potassium. It is a black powder, having the appearance of plumbago, and not apparently conducting electricity. It is difficultly soluble in the acids, with the exception of the hydrofluoric, which readily dissolves it, evolving hydrogen. Heated in the atmosphere, it readily burns into zirconia. Its equivalent, deduced from the analyses of Berzelius is about 22.

OXIDE OF ZIRCONIUM; ZIRCONIA; (*Zir* + *O*) was discovered in 1789



by Klaproth: it is of rare occurrence, having only been found in the *Zircon* or *Jargon* (whence the name of this earth.) The zircon is a *silicate of zirconia*, it is found in Ceylon, and occurs in some sienitic rocks: when colourless and transparent, it ranks among the gems: when coloured brown or red, it is termed *hyacinth* or *jacinth*, which also occurs in Ceylon, and is found in small crystals in the sand of the rivers of that island; also near Pisa in Italy; in Brazil, and elsewhere. These minerals contain about 70 *per cent.* of zircon, combined with silica and occasionally tinged by oxide of iron. (Klaproth, *Beiträge.*) Zirconia is obtained from them by the following processes. Reduce the colourless zircons to a fine powder, having previously heated them to redness, and quenched them in water. Mix the powder with nine times its weight of pure potassa, and gradually project it into a red-hot silver crucible, and keep it in perfect fusion for two hours. When the crucible has cooled, reduce the mass to a fine powder, and boil it in distilled water. Boil the undissolved residue in muriatic acid; filter, and evaporate to dryness; redissolve the dry mass in distilled water, and precipitate by carbonate of soda. The carbonate of zirconia which falls may be decomposed by heat.

The following method of obtaining pure zirconia is recommended by MM. Dubois and Silveira. (*Ann. de Chim. et Phys.*, xiv. 110.) Powder the zircons very fine, mix them with two parts of pure potassa, and heat them red-hot in a silver crucible for an hour. Treat the substance obtained with distilled water, pour it on a filter, and wash the insoluble part well; it will be a compound of zirconia, silica, potassa, and oxide of iron. Dissolve it in muriatic acid, and evaporate to dryness, to separate the silica. Re-dissolve the muriates of zirconia and iron in water; and to separate the zirconia which adheres to the silica, wash it with weak muriatic acid, and add it to the solution. Filter the fluid, and precipitate the zirconia and iron by pure ammonia; wash the precipitates well, and then treat the hydrates with oxalic acid, boiling them well together, that the acid may act on the iron, retaining it in solution whilst an insoluble oxalate of zirconia is formed. It is then to be filtered, and the oxalate washed, until no iron can be detected in the water that passes. The oxalate of zirconia is, when dry, of an opaline-colour; after being well washed, it is to be decomposed by heat in a platinum crucible. Thus obtained, the zirconia is perfectly pure, but is not affected by acids. It must be re-acted on by potassa as before, and then washed until the alkali is removed. Afterwards dissolve it in muriatic acid, and precipitate by ammonia. The hydrate thrown down, when well washed, is perfectly pure, and easily soluble in acids. (Other methods of proceeding are pointed out by Berzelius, *Lehrbuch*, i.)

Pure zirconia is a white infusible substance, insoluble in water, specific gravity 4.3. After having been heated to redness it scratches glass; it resists the action of the acids, with the exception of the sulphuric, and according to Berzelius, the best method of rendering it soluble consists in mixing it in fine powder with sulphuric acid, diluted with its weight of water, and heating the whole in a platinum crucible till the acid is evaporated, but not to redness: the *sulphate of zirconia* thus obtained is soluble in hot water.

HYDRATE OF ZIRCONIA may be thrown down from this solution by

caustic ammonia in the form of a bulky gelatinous precipitate, which if dried, or even washed with boiling water, loses its easy solubility; when exposed to a red-heat it becomes remarkably luminous after it has lost its water. This hydrate is sparingly soluble in the alkaline carbonates, and consists of 2 atoms of zirconia and 1 of water; zirconia being composed of

						Berzelius.
Zirconium	. 1	..	22	..	73.3	.. 73.686
Oxygen	. . 1	..	8	..	26.7	.. 26.314
	1		30		100.0	100.000

CHLORIDE OF ZIRCONIUM is obtained in the form of a white fixed compound, by heating zirconium in chlorine. Hydrated zirconia dissolves readily in muriatic acid, and the solution yields, on evaporation, small acicular silky crystals of *hydrated chloride*, soluble in water and in alcohol, but only sparingly soluble in muriatic acid. The anhydrous chloride cannot be obtained pure by heating the hydrate, for in that case it loses half its chlorine in the form of muriatic acid, whilst half the zirconium becomes zirconia.

FLUORIDE OF ZIRCONIUM. Zirconia dissolves readily in hydrofluoric acid, and yields, by slow evaporation, a crystallized salt, which, by the action of water, is resolved into a sub and super-salt. When solution of fluoride of potassium is added to excess of fluoride of zirconium, the solution yields, on evaporation, small granular crystals, sparingly soluble in cold water, of *potasso-fluoride of zirconium*, consisting, according to Berzelius, of

Potassium	. . . . 1	..	40	..	29
Zirconium	. . . . 2	..	44	..	32
Fluorine	. . . . 3	..	54	..	39
	1		138		100

When solution of fluoride of zirconium is dropped into excess of fluoride of potassium, an analogous triple compound is formed, containing 2 atoms of potassium, 3 of zirconium, and 5 of fluorine. (Berzelius.)

NITRATE OF ZIRCONIA is a very soluble and uncrystallizable compound: its solution dissolves hydrate of zirconia, and it is only imperfectly decomposed by the addition of alkalis.

SULPHURET OF ZIRCONIUM is formed by heating sulphur and zirconium in an exhausted vessel, or in an atmosphere of hydrogen; in both cases light is emitted, and a pulverulent brown sulphuret formed. It is insoluble in nitric, muriatic, and sulphuric acid, feebly acted on by nitromuriatic acid, but dissolved and decomposed by hydrofluoric acid.

SULPHATE OF ZIRCONIA. (ZIR + S'.) This salt is formed by digesting zirconia with sulphuric acid and a little water; the mixture must ultimately be heated nearly to redness: the remaining sulphate is readily soluble in boiling water, and yields, on evaporation, a gum-like mass, with no traces of crystallization; but if it be redissolved in sulphuric acid, the solution yields crystals which are still a neutral sulphate, and which may be freed from adhering acid by washing with alcohol: they contain water of crystallization. Berzelius has also described a *disulphate*, a *tris-sulphate*, an *ammonio-sulphate*, and a *potassa-sulphate of zirconia*.

PHOSPHATE and CARBONATE OF ZIRCONIA are insoluble salts.

CHARACTERS OF THE SALTS OF ZIRCONIA. These salts have an astringent taste: they are precipitated by caustic potassa, and the precipitate is not soluble in excess of the alkali. When boiled with sulphate of potassa a subsalt of zirconia subsides. Infusion of galls produces in them a yellow precipitate, and phosphate of soda throws down a white phosphate of zirconia. The recently-precipitated carbonate of zirconia is soluble in excess of bicarbonate of ammonia, or of potassa.

### § XXXIX. YTTRIUM.

IN 1794, Professor Gadolin discovered a new earth in a mineral from the quarry of Ytterby, in Sweden, to which Ekeberg, in 1797, gave the name of *Yttria*. The mineral has since been termed *Gadolinite*. It is composed of yttria, silica, and the oxides of iron and cerium. The following process for obtaining pure yttria is described by Vauquelin, in the 36th volume of the *Ann. de Chim.*; p. 150. (Henry, ii., 648.)

Fuse pulverized *Gadolinite* with twice its weight of potassa; wash the mass with boiling distilled water, and filter. The filtered solution, which has a beautiful green-colour, yields, during evaporation, a black precipitate of oxide of manganese. When this has ceased to appear, allow the liquor to stand; decant the clear part, and saturate with nitric acid. Let the insoluble part be also digested with extremely dilute nitric acid, which will take up the soluble earths only, and will leave undissolved the silica and oxide of iron. Let the two portions be mingled together, and evaporated to dryness; then re-dissolved and filtered; by which means any remains of silica and oxide of iron are separated. To obtain the yttria from the nitric solution, it would be sufficient, if no other earth were present, to precipitate it by carbonate of ammonia; but small portions of lime, and of oxide of manganese, are still present along with it. The first is separated by a few drops of carbonate of potassa; and the manganese by the cautious addition of hydro-sulphuret of potassa. The yttria is then to be precipitated by pure ammonia, washed abundantly with water, and dried. It amounts to about 35, or, according to Berzelius, 45 *per cent.* of the weight of the stone. It has been found also to form about one-fifth of the weight of *yttrotantalite*, and about one-twelfth of that of *yttrocerite*; and it occurs in the minerals termed *Orthite* and *Pyrrorthite*, and in the *fluoride* and *phosphate of yttrium*.

Berzelius obtains yttria as follows: *Gadolinite* in fine powder is dissolved in nitromuriatic acid, and the solution decanted from the deposited silica: crystals of sulphate of potassa are then added to it, and it is left for 24 hours: in proportion as the fluid becomes saturated by the sulphate, a white or yellowish powder falls, which is a double sulphate of potassa and protoxide of cerium: this is separated, and the clear solution neutralized by caustic ammonia, and the oxide of iron thrown down by succinate of ammonia. The precipitate is separated by filtration, and the clear liquid precipitated by caustic ammonia, by which yttria (with a little oxide of manganese) is thrown down: the oxide of manganese may be separated by digesting this precipitate in a solution of carbonate of

ammonia, filtering, and boiling, by which carbonate of yttria separates: this, being dried and heated to redness, leaves yttria.

Wöhler obtained *yttrium* in 1828 by dissolving yttria in muriatic acid, evaporating to dryness, and acting upon the *chloride of yttrium* so obtained by potassium: by washing the residue of this action, the yttrium remains in the form of gray metallic scales, brittle, and resisting the action of air and water: when heated in air or oxygen it burns brilliantly into yttria, which shows slight marks of fusion; it dissolves in sulphuric acid and in solution of potassa, but not in ammonia: it combines with sulphur, selenium, and phosphorus. (*Phil. Mag. and Annals*, v., 393.) The equivalent of yttrium is probably 32.

**OXIDE OF YTTRIUM.** (*yt + O.*) Yttria is insipid, white, and without action on vegetable colours. Its specific gravity = 4.842. It is insoluble in water, but very retentive of it. Insoluble in pure alkalis, but readily soluble in carbonated alkalis. In carbonate of ammonia it is much less soluble than glucina. It forms salts which have a sweetish austere taste, and which have been little examined. They are decomposed by the pure alkalis, and by lime and baryta. Oxalic acid and oxalate of ammonia throw down a white curdy precipitate from the solutions of yttria. Ferrocyanuret of potassium occasions in them a gray granular precipitate; phosphate of soda a white gelatinous one; and tincture of galls throws down brown flocculi.

Yttria appears to consist of

							Berzelius.
Yttrium	. . .	1	..	32	..	80	.. 80.1
Oxygen	. . .	1	..	8	..	20	.. 19.9
		1		40		100	100.0

**CHLORIDE OF YTTRIUM** is soluble, deliquescent, and uncrystallizable.

**FLUORIDE OF YTTRIUM** is an insoluble compound; it occurs *native*, combined with the fluorides of cerium and calcium, in the vicinity of Fahlun.

**SULPHATE OF YTTRIA** is crystallizable and of a pale-pink hue: it is remarkable for its tardy solubility in water. It forms a double salt with sulphate of potassa.

**NITRATE OF YTTRIA** is deliquescent, but by spontaneous evaporation it may be obtained in colourless crystals.

**PHOSPHATE OF YTTRIA.** The neutral phosphate is insoluble, and fusible before the blowpipe. When it is dissolved in an acid, and precipitated by ammonia, a basic phosphate falls. A *native phosphate of yttria* occurs near Lindesness, in Norway. (See Berzelius, in respect to some peculiarities of this salt.)

**CARBONATE OF YTTRIA** is a light flocculent precipitate, sparingly soluble in excess of carbonic acid, and in the carbonated alkalis. It decomposes and slowly dissolves in the salts of ammonia: dissolved in carbonate of ammonia it affords a crystallizable *ammonio-carbonate of yttria*.

**CHARACTERS OF THE SALTS OF YTTRIA.** They have a sweet astringent taste, not unlike those of glucina: their specific gravity exceeds that of the other earthy salts: some of them, when crystallized, have an ame-

thystine tint, derived probably from a trace of manganese. They are thrown down of a white colour by ferrocyanuret of potassium, and by caustic potassa, and the precipitate is not soluble in excess of the precipitant. Carbonated alkalis, when added in excess, slowly redissolve the precipitate. The *sulphate* is the most characteristic salt.

§ XL. THORINUM.

THIS substance was discovered by Berzelius in 1828, in a rare and complex mineral, found in the Syenitic rock of the Isle of Lövön, near Brevig, in Norway. It contained about 58 *per cent.* of *thorina*, (Poggend., xvi., 387,) which was obtained as follows: the mineral in powder was digested in muriatic acid, which formed a gelatinous mass, which, evaporated to dryness, and digested in dilute muriatic acid, left silica. The muriatic solution was then freed from lead and tin, by a current of sulphuretted hydrogen, and the clear solution saturated by ammonia: this occasioned a precipitate, which was washed, dissolved in dilute sulphuric acid, and the solution evaporated to a small bulk; during this evaporation *sulphate of thorina* was deposited, which, being washed with a saturated solution of sulphate of potassa, was dissolved in boiling water, and decomposed by caustic potassa, which threw down the thorina in the state of a white powder. (*Ann. de Chim. et Phys.*, xliii., 5.)

By passing a current of dry chlorine over a mixture of thorina and charcoal-powder, a crystalline *chloride of thorinum* is obtained, which is easily decomposed by potassium, and the product is *thorinum*. It is of a gray colour, metallic lustre, and apparently malleable. It is not oxidized by hot or cold water, but when heated in the air it burns with great brilliancy into thorina, which is snow-white, and shows no traces of fusion. It is feebly acted on by sulphuric acid, and scarcely by nitric acid: it is not attacked by the caustic alkalis at a boiling heat. Muriatic acid dissolves it, with the evolution of hydrogen. Its apparent equivalent is 60. (59.6 Turner.)

OXIDE OF THORINUM. THORINA, (*th + o*,) obtained as above described, and after having been heated to redness, is white, and insoluble in the acids, with the exception of the sulphuric. When thrown down in the state of *hydrate* it dissolves readily, and exposed to the air absorbs carbonic acid. It probably consists of

Thorinum . . . . .	1	..	60	..	88
Oxygen . . . . .	1	..	8	..	12
	1		68		100.

Thorinum combines energetically with chlorine, sulphur, and phosphorus. The *chloride* has been above adverted to: the other compounds have been but imperfectly examined.

Thorina is distinguished from the other oxides by the following properties: from alumina and glucina by its insolubility in pure potassa; from yttria, by forming with sulphate of potassa a double salt, which is quite insoluble in a cold saturated solution of sulphate of potassa; from zirconia, by the circumstance that this earth, after being precipitated from a hot solution of sulphate of potassa, is almost insoluble in water and the

acids. Thorina is precipitated also by ferrocyanuret of potassium, which does not separate zirconia from its solutions. Berzelius has remarked that sulphate of thorina is much more soluble in cold than in hot water, so that a cold saturated solution becomes turbid when heated, and in cooling, recovers its transparency. (Turner's *Elements*, 511.)

### § XLI. ALUMINUM.

THE term *aluminum* or *aluminium* has been applied to the metallic base of the earth *alumina*, a substance of common occurrence in the mineral world, and of great importance in its applications to the arts. The nature of alumina was discovered by Davy in 1808, (*Elem. Chem. Phil.*, 355,) who found that potassa was generated by passing the vapour of potassium over white-hot alumina: he did not, however, determine the properties of its base. This has since been more accurately effected by Wöhler, to whom we owe the following ingenious method of obtaining it (*Ann. de Chim. et Phys.*, Jan. 1828, and Poggendorff, *Annalen*, xi., 146). *Chloride of aluminum* is heated with potassium in a small platinum crucible; the heat of a spirit-lamp is sufficient, for when the substances begin to act, the temperature suddenly rises to redness, and care should be taken so to adjust the relative proportions of materials, that none of the chloride may be evaporated in an undecomposed state, while at the same time there should not be excess of alkali in the residue. When the crucible is cold, its contents are well washed with cold water, by which a finely-divided gray substance, with a certain degree of metallic lustre, is obtained, which is pure aluminum.

*Aluminum* is extremely difficult of fusion; and although in the pulverulent state it does not apparently conduct electricity, it becomes a conductor when its particles are aggregated by heat. This, if not arising from imperfect contact, is an interesting fact, and holds good also, according to Wöhler, in the case of iron, which does not conduct when in very fine powder. Aluminum is not oxidized by exposure to air, but, when heated nearly to redness, it burns into a hard white substance, having the properties of alumina. When sprinkled into the flame of a spirit-lamp it scintillates like iron-flings, and if, when red-hot, it be immersed in oxygen, it burns with vivid light and intense heat: the result is fused alumina, apparently as hard as corundum.

Aluminum is not acted on by water at common temperatures, but when boiled it is slightly oxidized, and a little hydrogen is evolved: the oxidizement is, however, imperfect and superficial. It is not affected by nitric or sulphuric acids at common temperatures, but it rapidly dissolves in hot sulphuric acid, and sulphurous acid is evolved. The dilute acid dissolves it with the evolution of hydrogen, as is also the case with muriatic acid. It is soluble with the evolution of hydrogen in caustic ammonia and potassa, and alkaline solutions of alumina are the results.

There is much difficulty in determining the equivalent of aluminum, arising out of the different views that may be taken of the atomic constitution of *alumina*, which is its only known oxide: some chemists regard it as a *protoxide*, and in that case a number intermediate between 9 and 10 would represent aluminum; others, from the analogy that subsists

between some of the combinations of alumina and the peroxide of iron have regarded it as a sesquioxide; and here again a discrepancy in its equivalent ensues, dependent upon its being considered as composed of 1 of aluminum and 1.5 oxygen, or of 2 and 3. Gmelin has adopted the equivalent 9, and Thomson 10, regarding alumina as a protoxide: Dr. Turner, considering alumina as a sesquioxide, represents aluminum by the equivalent 13.7, and then doubles that number in order that alumina may be regarded as consisting of 2 equivalents of aluminum and 3 of oxygen: now  $12 : 13.7 :: 8 : 9.1$ , so that assuming alumina as a protoxide, Dr. Turner's number would be 9.1. The equivalent 10 is more consistent with the experimental results of Thomson and of Berzelius than 9, and is therefore that which I have adopted.

OXIDE OF ALUMINUM; SESQUIOXIDE OF ALUMINUM; ALUMINA. (*al* + *o*.) To obtain pure *alumina* we decompose a solution of pure *alum* by excess of carbonate of potassa, wash the precipitate with repeated portions of hot distilled water, redissolve it in muriatic acid, precipitate it again by ammonia, thoroughly eduleorate, and dry the precipitate: it is rendered anhydrous by exposure to a red-heat. Pure alumina may also be obtained according to Gay Lussac (*Ann. de Chim. et Phys.*, v. 102,) by igniting *ammonia-alum*, previously deprived of water of crystallization by heat: sulphate of ammonia evaporates, and alumina remains, perfectly white, and very soft to the touch. It readily blends with water, but assumes its former properties after having been gently heated. Its extreme division, and the hardness of its particles, observes Gay Lussac, might render it useful for polishing metal, and its whiteness for the preparation of colours.

Alumina is a colourless, insipid, insoluble powder, without action upon vegetable blues: its specific gravity is 2. It has a strong attraction for moisture, which it rapidly absorbs from humid air, to the amount of one-third its own weight. When precipitated from its solution, and dried at a temperature of  $60^{\circ}$ , it retains about half its weight of water; this may be expelled by ignition. When mixed with water, alumina is characterized by the plasticity of the mixture; and if the paste be dried in the air, and then heated, it shrinks considerably in consequence of the loss of water; this shrinkage was applied by Wedgwood to pyrometrical purposes. Alumina has a strong affinity for various organic compounds, and its use in the arts of dyeing and calico-printing depends upon its attraction for different colouring-principles, and for ligneous fibre. If ammonia be added to a solution of alum in infusion of cochineal, or of madder, the aluminous earth falls in combination with the red colouring-matter, and the supernatant liquor remains colourless. Colours thus prepared are called *Lakes*.

Moist alumina is readily soluble in most of the acids; but after the expulsion of its water by a red-heat, it is much more difficultly dissolved. It is very sparingly soluble (when moist) in caustic ammonia; but potassa and soda readily dissolve it, and it is also soluble, to a certain extent, in the aqueous solutions of baryta and strontia. The fixed alkaline solutions of alumina are decomposed by the acids and by ammoniacal salts. Some of the earthy combinations of alumina exist *native*, and in them it has been regarded as performing the part of an acid; so that they

have been called *Aluminates*. Alumina is recognised by its solubility in caustic potassa; by the formation of octoëdral crystals of alum on evaporating its sulphuric solution with the addition of sulphate of potassa; and by the fine blue colour which it affords when moistened with nitrate of cobalt and strongly heated: this, according to Berzelius, is the most certain test.

The different *hydrates of alumina* have been referred to distinct atomic compounds, but their composition has not been satisfactorily ascertained: they occasionally occur *native*. Regarding alumina as a protoxide, it consists of

				Berzelius.	Davy.						
Aluminum	.	1	..	10	.	55.5	..	53.3	..	56	
Oxygen	.	.	1	..	8	..	44.5	..	46.7	..	44
		—		—		—	100.0	—	100.0	—	100

*Native Alumina* may be said to constitute the *sapphire*, which occurs either colourless or pale-blue, is extremely hard, and occasionally crystallized: its specific gravity is about 4. The oriental *ruby* and the oriental *topaz* are red and yellow varieties of sapphire. These gems are mostly found in alluvial deposits in Ceylon and Pegu: they have also been met with in France and Bohemia. *Corundum*, *adamantine spar*, and *emery*, are minerals also consisting chiefly of alumina, with less than 2 per cent. of oxide of iron, and a little silica. All these substances are extremely hard, being, in that respect, second only to diamond.

**CHLORIDE OF ALUMINUM.** (*al + c.*) This compound has been mentioned as a source of *aluminum*; it was obtained by Wöhler, as follows: Alumina, in the state of pulverulent hydrate, is mixed into a paste with powdered charcoal, oil, and sugar, and this is heated in a covered crucible till the organic matter is destroyed: an intimate mixture of the earth with charcoal is thus obtained, which is introduced whilst hot, into a proper porcelain or glass tube, placed in a convenient furnace: dried chlorine is then passed through it into a receiver attached to the other end of the tube, and the air being thus expelled, the tube is heated red-hot, and chlorine gradually passed into it: carbonic oxide is disengaged, and chloride of aluminum formed, which chiefly collects within the tube, and ultimately plugs it up. It is a crystalline translucent substance of the colour of chlorine; it fumes and deliquesces when exposed to air, and is energetically acted upon by water, which yields a solution of *muriate of alumina*. It is probably a compound of one proportional of each of its constituents.

**CHLORATE OF ALUMINA** is a deliquescent salt.

**IODIDE AND BROMIDE OF ALUMINUM** have not been examined.

**FLUORIDE OF ALUMINUM.** Hydrate of alumina readily dissolves in hydrofluoric acid, and, on evaporation, a gummy substance is obtained, which bears a red-heat without entire decomposition. Berzelius has described two *alumino-fluorides of potassium* obtained from mixed solutions of the two fluorides. *Alumino-fluoride of sodium* occurs native in *Kryolite*, a rare mineral hitherto found only in Greenland.

**NITRATE OF ALUMINA** is very difficultly crystallizable, and generally obtained, on evaporating its solution, in the form of a semitransparent



gum-like mass, very deliquescent, and soluble in alcohol. When decomposed by caustic ammonia, a pasty precipitate separates, which is a *subnitrate*, not decomposed by excess of ammonia. (Berzelius.)

SULPHURET OF ALUMINUM ( $al + S$ ) is obtained by dropping sulphur upon incandescent aluminum, or by passing the vapour of sulphur over red-hot aluminum. A black compound is the result, which is decomposed by exposure to air, and which, when thrown into water, deposits alumina, and evolves sulphuretted hydrogen: it probably, therefore, contains one proportional of each of its components.

SULPHATE OF ALUMINA ( $Al + S'$ ) is formed by digesting hydrate of alumina in sulphuric acid, diluted with an equal bulk of water: the solution is evaporated and alcohol added, which throws down the sulphate. It dissolves in two parts of water, and forms small lamellar crystals, of a sweet and astringent taste. Exposed to heat, this salt loses water of crystallization to the extent of 46.6 *per cent.*, and an *anhydrous sulphate* remains. By long exposure to a red-heat, the whole of the acid is expelled. This salt may be used as a test for potassa; for when it is dropped into a strong solution of that alkali or its salts, alum is thrown down. It consists of

Alumina . . . . .	1		18		31
Sulphuric acid . . . . .	1		40		69
	1		58		100

The crystallized salt contains

Alumina . . . . .	1		18		16.1				
Sulphuric acid . . . . .	1		40		35.7			..	53.4
Water . . . . .	6		54		48.2			..	46.6
	1		112		100.0		100.0		

#### SULPHATE OF ALUMINA AND POTASSA; COMMON ALUM; POTASH ALUM.

$3 (Al + S') + (P + S') + 25 Q$ . This useful salt is manufactured upon an extensive scale in Britain. *Aluminous slate*, which is argillaceous slaty rock, containing sulphuret of iron, is roasted so as to oxidize the iron and acidify the sulphur: on lixiviating the roasted ore, a *sulphate of alumina* is obtained, which, with the addition of *sulphate of potassa*, yields alum. The *shales* or wastes of old coal-mines, which fall down in a decaying or decomposing state, yield, on lixiviation, considerable quantities of sulphate of alumina and sulphate of iron: the solution of these salts is evaporated at the alum-works, near Glasgow, in large brick cisterns, by carrying the flue of a furnace over its surface, and, when sufficiently concentrated, is run out into coolers, where the sulphate of iron crystallizes, and the sulphate of alumina, being the much more soluble salt, remains in the mother-liquors: to these, sulphate of potassa is added, and they then yield crystals of alum, not at first pure, but rendered so, and obtained in beautifully-perfect octoëdral crystals, by recrystallization. The sulphate of potassa, required for this manufacture, is obtained by burning common sea-weed, collected upon the coast; the ash, or *kelp*, contains salts of potassium, which are purified by crystallization: the mother-liquors, which were formerly thrown away, are now resorted to as sources of *iodine*.

Alum has a sweet and astringent flavour, accompanied by some degree of acidity: it reddens vegetable blues; it dissolves in about five parts of cold water, and in rather more than its own weight of boiling water. The crystals, when heated, readily fuse in their water of crystallization, and when this is expelled by the application of a sufficient temperature, the dry alum becomes opaque and spongy, and in this state is generally termed *burned alum*. At a red-heat alum loses a portion of its acid. In its *crystallized* state, alum consists of

Sulphate of alumina . . . . .	3	..	174	..	35.73
Sulphate of potassa . . . . .	1	..	38	..	18.07
Water . . . . .	25	..	225	..	46.20
	<hr/>		<hr/>		<hr/>
	1		487		100.0

Or,

				Berzelius.	Thomson.
Alumina . . . . .	3	..	54	..	11.08
Potassa . . . . .	1	..	48	..	9.85
Sulphuric acid . . . . .	4	..	160	..	32.62
Water . . . . .	25	..	225	..	46.45
	<hr/>		<hr/>		<hr/>
	1		487		100.00
					<hr/>
					100.00
					<hr/>
					100.00

HOMBERG'S PYROPHORUS. When potash-alum is ignited with charcoal, a spontaneously-inflammable compound results, which has long been known under the name of *Homberg's pyrophorus*. The potassa is decomposed in this process, along with the acid of the alum, and pyrophorus is probably a compound of sulphur, charcoal, and potassium, with alumina.

Pyrophorus is most successfully prepared by the following process. Mix equal parts of honey, or of brown sugar and powdered alum, in an iron ladle, melt the mixture over a fire, and keep it stirred till dry: reduce the dry mass to powder, and introduce it into a common phial coated with clay, and placed in a crucible of sand. Give the whole a red-heat, and when a blue flame appears at the neck of the phial, allow it to burn about five minutes, then remove it from the fire; stop the phial, and allow it to cool, taking care that air cannot enter it. (See SULPHATE OF POTASSA.)

SULPHATE OF ALUMINA AND AMMONIA; AMMONIA-ALUM. [ $3(Al + S') + (A + S') + 25Q.$ ] This salt is obtained exactly as the preceding, only *sulphate of ammonia* is substituted for sulphate of potassa: its atomic constitution also resembles that of potash-alum, and it is so similar in other respects, that as far as mere appearance and more obvious properties are concerned, the two salts are not readily distinguished. This variety of alum was formerly much in use, and the requisite ammonia was chiefly derived from putrid urine. When heated it loses water, then ammonia, and at a very high heat, its acid.

SULPHATE OF ALUMINA AND SODA; SODA-ALUM. [ $3(Al + S') + (S + S') + 25Q.$ ] In this salt *sulphate of soda* takes the place of the sulphate of potassa in the common alum: it crystallizes in octoëdra, which are less hard and regular than those of potash-alum, and effloresce in a dry air. (*Quart. Jour.*, viii., 386.) It dissolves in about its own weight of water.

**SULPHATE OF ALUMINA AND IRON.** This salt forms white silky crystals or fibres, composed of 4 atoms of sulphuric acid, 3 of protoxide of iron, 1 of alumina, and 25 of water. (Phillips, *Ann. of Phil.*, v.)

Some other double salts of alumina (subsals,) have been described by Riffault. (*Ann. de Chim.*, xvi., 355.)

**PHOSPHURET OF ALUMINUM** is formed by passing the vapour of phosphorus over red-hot aluminum. Exposed to air it smells of phosphuretted hydrogen, and it decomposes water. (Wöhler.)

**PHOSPHATE OF ALUMINA** is insoluble in water, but it dissolves in phosphoric acid, and yields, on evaporation a gummy deliquescent compound. When excess of ammonia is added to an acid solution of the phosphate, a *subphosphate of alumina* is precipitated, which is soluble in caustic potassa. The mineral called *Wavellite* is a *hydrated subphosphate of alumina*, consisting of 2 atoms of alumina, 1 of phosphoric acid, and 3 of water. The rare mineral, called *ambligonite*, found at Chirnsdorff, in Saxony, is a double *phosphate of alumina and lithia*. (Berzelius.)

**SELENIURET OF ALUMINUM** is a black pulverulent compound, rapidly decomposed by water.

**BORATE OF ALUMINA** may be formed by boiling recently-precipitated alumina with boracic acid: it is uncrystallizable, and of a very astringent taste.

**ALLOYS OF ALUMINUM.** Aluminum probably exists in some of the varieties of cast-iron and steel. By fusing highly-carburetted steel with alumina, a peculiar alloy results, which is white, granular, and brittle, and which yields, on analysis, 6.4 *per cent.* alumina. On fusing 67 parts of this alloy with 500 of steel, a compound is obtained, which possesses all the characters of the best Bombay *wootz*, and like it, when its surface is polished and washed over with dilute sulphuric acid, exhibits the striated appearance called *damask*, for which the celebrated sabres of Damascus are remarkable, and which renders it probable that they also are made of *wootz*. (*Quarterly Journal of Science and Arts*, ix.)

**CHARACTERS of the SALTS OF ALUMINA.** These salts have an astringent, sweet, and subacid taste: they are precipitated by the caustic fixed alkalis, but the precipitate is redissolved when they are added in excess. Sulphate of potassa, with a little sulphuric acid, added to a strong solution of alumina, throws down a white powder, which is *alum*: phosphate of soda produces a white flocculent precipitate of phosphate of alumina. Succinate of ammonia and infusion of galls occasion precipitates in strong aluminous solutions.

## § XLII. SILICIUM.

FROM experiments upon the action of potassium upon *silica*, Sir H. Davy concluded that that earth consisted of a peculiar inflammable basis, combined with its weight of oxygen, and he called the basis *Silicium*.

This estimate of the composition of silica was deduced from the quantity of potassium required for its decomposition; the subject has since received further elucidation, and the correctness of the above statement has, to a great extent, been confirmed.

In the year 1824, silicium was obtained in its pure state by Berzelius,

and from its properties, presently to be described, he has placed it, correctly perhaps, among the simple non-metallic combustibles; indeed, it bears a strong resemblance to boron. Before, however, we remove it from the class of bodies with which it has usually been associated, it may be well to wait till its general characters have been more satisfactorily studied. From the ample account of this substance, given by Berzelius, the following details are chiefly extracted.

He recommends, as the best source of silicium, the *silico-fluoride of potassium*, which is prepared by passing silico-fluoric acid into a solution of potassa, evaporating to dryness, and heating the residue nearly, but not quite, to redness. The salt thus obtained is to be well mixed with eight or nine-tenths its weight of potassium, and the mixture introduced into a green glass tube and heated: before it acquires a red-heat, its contents become ignited, in consequence of the chemical action that ensues, and the potassium is burned at the expense of the silica; a brown mass is thus obtained, consisting of fluoride of potassium, siliciuret of potassium, and a portion of the undecomposed salt: this is thrown into cold water, which occasions the evolution of hydrogen, resulting from the action of the siliciuret, the potassium of which is converted into potassa, and the silicium set free. When the effervescence is over, and the fluid has become clear, it is poured off from the residue, which is again washed, allowed to subside, and separated by decantation as before. These first washings must be performed with cold water, otherwise the alkali re-acts on the silicium, which, however, may now be thoroughlyedulcorated with boiling water. It remains in the form of a dark-brown powder, infusible, and a non-conductor of electricity. Its properties are remarkably different before and after the application of a red-heat: *before it has been heated* it burns easily in the air; but the superficial formation of silica prevents its entire combustion: in oxygen it burns brilliantly, and however carefully prepared, it always produces a little moisture. It is not acted upon either by sulphuric, nitric, or nitromuriatic acids, even when aided by heat. Liquid hydrofluoric acid readily dissolves it, evolving hydrogen: it is also dissolved when heated in a solution of caustic potassa. Silicium, *after it has been heated* (obtained, for instance, by washing that which has been partially burned in the air, with hydrofluoric acid, to remove the superficial silica), sinks in sulphuric acid, is incombustible before the blowpipe and in oxygen, and is not acted on by hydrofluoric acid, nor by caustic potassa; but it is easily dissolved in a mixture of hydrofluoric and nitric acids.

Silicium may be perfectly oxidized, and entirely converted into *silica* or *silicic acid* by mixing it with dry carbonate of potassa, and heating to redness; it burns at the expense of the oxygen of the carbonic acid, and a *silicate of potassa* is obtained. Fused nitrate of potassa has no action upon it; but the addition of a little dry carbonate of potassa causes immediate deflagration: this paradoxical appearance depends upon the circumstance that the attraction of silicium for oxygen is influenced by the presence of the alkali, which has a high attraction for silica; just as the effect of zinc upon water is influenced by the presence of an acid, having an attraction for the oxide of zinc about to be produced. Carbonic acid is so weak that it does not prevent the action of

the alkali: and as silicium has a much stronger attraction for oxygen than carbon, it is oxidized at the expense of the carbonic acid. Nitric acid, on the other hand, is a strong acid, which entirely prevents this action of the alkali in the saltpetre, upon the silicium; and silicium, at the temperature at which saltpetre fuses does not become oxidized; but if the heat be raised to whiteness, the silicium is then speedily oxidized by the decomposition of the nitric acid, and intense combustion ensues. Heated with the caustic alkalis, silicium burns in the oxygen of the water which they contain.

The equivalent of silicium has been variously estimated; according to Berzelius, silica is composed of 51.6 oxygen, and 48.4 silicium, and regarding it as a *protoxide*, this would give 7.5 as the equivalent of silicium, for  $51.6 : 48.4 :: 8 : 7.5$ . But Berzelius considers silica as a compound of 1 atom of base + 3 oxygen, hence 22.5 is his equivalent of silicium, and silica would be represented by  $(Si + 3O)$ , or  $22.5 + 24 = 46.5$ . Dr. Thomson, whose views I shall adopt, regards silica as a protoxide, and as composed of equal weights of base and oxygen, so that the equivalent of silicium will be identical with that of oxygen, or 8.

OXIDE OF SILICIUM, SILICA, or SILICIC ACID,  $(Si + O) Si$ , or  $Si'$ , is a very abundant natural product. It exists pure in some varieties of *rock-crystal*, and nearly pure in *flint*\*. It may be obtained by heating

\* The following are the principal minerals containing silica pure or nearly so.

i. *Rock-crystal* or *Quartz*, which may be considered as pure silica. It crystallizes in the form of a six-sided prism, ended by six-sided pyramids; some varieties are perfectly transparent and colourless; others white and more or less opaque. Its specific gravity is 2.6. It is so hard as to give sparks when struck with steel, and is nearly infusible. The primitive crystal, which is very rare, is an obtuse rhomboid, the angles of which are  $94^{\circ} 24'$ , and  $85^{\circ} 36'$ . The finest specimens are brought from Madagascar and the Alps. The perfectly transparent crystals found near Bristol, and in Cornwall, are sometimes called *Bristol* and *Cornish diamonds*. The fine crystals are cut into ornaments, and sometimes used as a substitute for glass in spectacles; they are then termed *pebbles*, and do not so readily become scratched as glass.

*Brown and yellow crystals of Quartz* are found in great beauty in the mountain of Cairn Gorm, in Scotland, and are much admired for seal-stones, &c.: they are sometimes improperly termed topazes.

*Purple quartz* or *amethyst*, is tinged with a little iron and manganese. *Rose quartz* derives its colour from manga-

nese. *Prase* or *green quartz*, contains actinolite; and *chrysoprase* is tinged of a delicate apple-green by oxide of nickel. *Avanturine* is a beautiful variety of quartz, of a rich brown colour, which, from a peculiarity of texture, appears filled with bright spangles; the finest specimens are from Spain: it is often imitated. Small crystals of quartz, tinged with iron, are found in Spain, and have been termed *Hyacinths of Compostella*.

ii. *Flint*, *Chalcedony*, *Carnelian*, *Onyx*, *Sardonyx*, and *Bloodstone* or *Heliotrope*, and the numerous varieties of *Agates*, are principally composed of quartz, with various tinging materials.

iii. *Opal* is among the most beautiful productions of the mineral world; it is a compound of about 90 silica and 10 water, and is distinguished by its very brilliant play of colours. The finest specimens come exclusively from Hungary. There is a variety of opal called *Hydrophane*, which is white and opaque till immersed in water; it then resembles the former.

*Common opal* is usually of a dirty white, and does not exhibit the colours of the noble opal; it contains silica and water, with a little oxide of iron, and is not of unfrequent occurrence. The substance called *menilite* from Menil Montant, near Paris, is nearly allied to

colourless rock-crystal to redness, quenching it in water, and reducing it to a fine powder; in this state it is silica almost perfectly pure. "Fuse one part of this powder with three of potassa in a silver crucible. Dissolve the mass formed, in water, add slight excess of muriatic acid, and evaporate to dryness. Wash the dry mass in boiling distilled water upon a filter, and the white substance which remains is silica." This is the usual process; but the earth obtained by simply reducing the colourless rock-crystal to powder, is more pure; it only contains a trace of oxide of iron and manganese, and of alumina. It is very difficult to separate the last portions of alkali from silica precipitated from potassa. A very pure silica may be obtained, by the fusion of fine white sand, or powdered rock-crystal, with carbonate of lime: the resulting compound of lime and silica may be decomposed by dilute muriatic acid; and the silica, after having been duly washed, is in the form of a very light powder. When silico-fluoric gas is passed into water, the silica which is precipitated, after having been washed and dried, is also very pure, and in a state of extreme mechanical division.

Silica, in its ordinary state, is a harsh white powder, insoluble in water and in most other solvents, and infusible except in the intense heat of the flame of a spirit-lamp, urged by the oxygen blowpipe: it then melts with difficulty into a colourless globule. Its specific gravity is 2.66.

When recently precipitated, and in the state of *hydrate*, it is to a certain extent soluble in water and in the acids. The aqueous solution is tasteless, and, when evaporated, deposits gelatinous silica, which, on being dried, becomes again quite insoluble: the acid solutions also exhibit no indication of saline combination, but when evaporated leave pure silica. Silica is often found in spring and mineral water; and in the fountains of Reikum and the boiling Geysers of Iceland it is contained in such quantities as to be deposited by them in the form of a porous incrustation. According to the view of the atomic constitution of silica above suggested, it will consist of

				Berzelius.
Silicium . . . . .	1	..	8	50
Oxygen . . . . .	1	..	8	50
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	1		16	100
				<hr style="width: 100%;"/>
				100.0

CHLORIDE OF SILICIUM. (*Si + Cl*.) Silicium burns when heated in chlorine, or when a current of chlorine is passed over red-hot silicium in a porcelain tube, and a fuming liquid is the result; of a yellow colour, extremely volatile, and irritating to the nose and eyes, and which, exposed to moist air, forms muriatic acid and silica. Dropped into water it floats upon that fluid, and is then dissolved, depositing a little gelatinous silica: muriatic acid is also formed. When potassium is heated in its vapour, it burns with the production of siliciuret and chloride of potassium. It consists of

common opal. It is found in irregular masses in a bed of clay.

iv. *Pitchstone*, so called from its resinous appearance, contains 73 *per cent.* of silica. *Obsidian*, a volcanic pro-

duct, contains 78 *per cent.* of silica, and much resembles glass in appearance; and the different kinds of *pumice* are nearly of similar composition.

				Berzelius.
Silicium . . . . .	1	..	8	.. 18.3
Chlorine . . . . .	1	..	36	.. 81.7
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	1		44	100.0
			<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
			100.0	100.0

IODIDE OF SILICIUM has not been formed.

BROMIDE OF SILICIUM (*Si + b*) was obtained by Serullas by passing the vapour of bromine over heated silicium: it is a colourless fuming liquid, heavier than sulphuric acid. It congeals at 10° and boils at 300°. It is decomposed when gently heated with potassium, with explosive violence; water converts it into hydrobromic acid and silica. (*Phil. Mag. and Ann.*, xi., 395.)

FLUORIDE OF SILICIUM. The only acid body which acts energetically upon silica is the hydrofluoric acid. The result of this action is a gaseous compound, which has been called *silicated fluoric acid*, or *fluo-silicic acid*; it is probably a binary compound of silicium and fluorine.

To obtain this gaseous compound, three parts of fluor-spar and two of powdered glass, or of silica finely powdered, are mixed in a retort with about an equal weight of sulphuric acid; the gas evolved is to be collected over mercury, and when its production slackens, it may be accelerated by a gentle heat. The mercury and the glass vessels employed must be quite dry.

Silicated fluoric acid is a colourless gas; its odour is acrid, much resembling muriatic acid; its taste very sour; its specific gravity is 3.61 compared with air: 100 cubic inches weigh about 112 grains. It extinguishes the flame of a taper. It produces white fumes when in contact with damp air; and when exposed to water it is absorbed, and a soluble compound of silica with fluoric acid is formed; whilst a quantity of silica is at the same time precipitated. If the beak of the retort from which the gas is issuing be plunged into a basin of water, it is soon choked by the copious deposit of hydrated silica, which sometimes forms tubes through the water, by which the gas escapes directly into the air. When it is intended to saturate water with the gas (it takes up about 260 volumes), this effect may be prevented by agitation, or better by suffering the gas to escape through a stratum of mercury into water above it.

Water thus saturated becomes a gelatinous mass, from which the acid liquor may be separated, by placing it, without pressure, upon a linen filter. The liquor is sour, and, when saturated with the fixed alkalis, becomes gelatinous, but not turbid: with barytic salts it soon deposits a white precipitate. Saturated with potassa, and evaporated to dryness, it yields the *silico-fluoride of potassium*, already adverted to as a source of silicium. It is a hydrated silico-fluoric acid, and when evaporated, gaseous fluoride of silicium escapes, and hydro-fluoric acid is evolved, so that, although the original aqueous solution does not act upon glass, it immediately does so when so far concentrated by evaporation as to generate the free hydrofluoric acid.

When one volume of silicated fluoric acid is mixed with two of ammonia, a total condensation ensues, and a dry *silico-fluate of ammonia* results, which is decomposed by the action of water. When silico-fluoric gas is passed into liquid ammonia, the whole of the silicium is

separated in the form of silica, and hydrofluoric acid of ammonia remains in solution. Potassium heated in this gas, burns, and produces silico-fluoride of potassium.

Fluoride of silicium consists of

					J. Davy.	Berzelius.				
Silicium	. . . . .	1	..	8	..	30.8	..	30.7	..	29.32
Fluorine	. . . . .	1	..	18	..	69.2	..	69.3	..	71.68
		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
		1		26		100.0		100.0		100.00

SILICO-FLUORIDE OF POTASSIUM. ( $po + 2si + 3f.$ ) When this salt is formed by passing silicated fluoric acid into a solution of potassa, it falls in the form of an iridescent jelly which dries into a white powder, very sparingly soluble in boiling water, and yielding minute anhydrous crystals. It appears that in the formation of this salt the potassa acting on the hydrofluoric acid forms fluoride of potassium, which combines with the fluoride of silicium, in the proportion of 1 equivalent of the former to 2 of the latter; or that silico-fluoride of potassium consists of

Potassium	. . . . .	1	..	40	..	36.4
Silicium	. . . . .	2	..	16	..	14.6
Fluorine	. . . . .	3	..	54	..	49.0
		<hr/>		<hr/>		<hr/>
		1		110		100.0

SILICO-FLUORIDE OF SODIUM is obtained in the same way as the potassium salt, but falls more readily, and is not iridescent: it is more soluble, especially in hot water. It may be obtained in small shining crystals, which are anhydrous hexangular prisms.

SILICO-FLUORIDE OF BARIUM is gradually precipitated when silico-fluoric acid is mixed with chloride of barium, in anhydrous microscopic crystals, of difficult solubility in water.

The *silico-fluorides of strontium, calcium, magnesium, and lead* are formed by dissolving their carbonates in silico-fluoric acid. The salts of magnesium and of lead are very soluble. The *silico-fluorides of manganese, iron, zinc, cobalt, nickel, and copper*, are soluble in water, and crystallize in similar hexagonal prisms, probably isomorphous, which contain respectively 1 equivalent of the silico-fluoride, and seven equivalents of water of crystallization.

SULPHURET OF SILICIUM. Silicium when heated intensely, burns brilliantly in the vapour of sulphur, and a white earthy compound is the result, which is not affected by dry air, and when heated to redness is slowly decomposed, with the production of sulphurous acid. It is rapidly decomposed by water; in moist air it exhales sulphuretted hydrogen, and that gas is abundantly evolved by its action on water, whilst the silica is retained in aqueous solution, and no sulphur is deposited: hence it consists of

					Berzelius.			
Silicium	. . . . .	1	..	8	..	33.5	..	30
Sulphur	. . . . .	1	..	16	..	66.5	..	70
		<hr/>		<hr/>		<hr/>		<hr/>
		1		24		100.0		100.

PHOSPHURET OF SILICIUM has not been formed.

CARBURET OF SILICIUM. When the potassium employed in the reduction of silica contains carbon, the resulting silicium is partly in the



state of *carburet*; it has a dark colour, and gives off carbonic acid when burned.

**ALLOYS OF SILICIUM.** Berzelius remarks that silicium only combines with the metals when in its nascent state, and that when once insulated no such compounds can be formed. When silica is reduced in contact of platinum, it becomes penetrated by silicium; but silicium may afterwards be heated white-hot in a platinum crucible without any such effect.

**SALTS OF SILICIUM.** It is obvious from the preceding statement, that there are no salts, properly so termed, in which the oxy-acids are combined with silica, but that silicium forms haloid compounds. But silica readily combines in the manner of an oxide or acid, with many of the salifiable bases; hence the term *silicic acid* applied to it, and *silicates* to its compounds. Of these compounds several are most importantly useful, and many of them are found as natural products, forming crystallized minerals, and parts of the strata or rocks that constitute the exterior crust of our globe. Glass, pottery, and porcelain, in all their varieties, are combinations of silica, and it is an essential ingredient in soils. I shall first describe some of the best-defined silicates, and then advert to the manufactures in which it is concerned, and conclude with an outline of the nature and composition of soils.

**SILICATE OF POTASSA.** When 1 part of silica and 4 of caustic potassa are fused together, and slowly cooled, a part of the compound may be poured out of the crucible before the whole has solidified, and pearly crystals are formed in the residuary portion, which are apparently composed of 1 atom of silica and 1 of potassa. (Berzelius.) When 1 part of silica and 2.5 of carbonate of potassa are fused together, the carbonic acid is expelled, and a *bisilicate of potassa* is the result. (H. Rose.) These silicates are soluble in water, forming the *liquor silicum* of the older chemists. This solution may also be obtained by digesting gelatinous hydrate of silica, or very finely divided silica in solution of potassa: the silica is thrown down from these solutions in the gelatinous state, by the acids. When potassa and great excess of silica are fused together, a species of *glass* is the result, which however is still acted upon by water; this solubility is greatly impaired by the presence of lime and alumina. The atomic composition of the different vitreous compounds that may be thus formed, cannot be ascertained, but they generally contain from 15 to 20 equivalents of silica to 1 of potassa. When 15 parts of silica, 10 of carbonate of potassa, and 1 of powdered charcoal, are fused together for about six hours, a vitreous compound is obtained, which when dissolved by boiling in water, filtered, and concentrated by evaporation, may be used to render wood, paper-hangings, scenery, and other such articles, incombustible: it may be mixed with alumina or chalk, and applied in the manner of a paint. (Fuchs., Schweigger's *Journal*, xxiv., 378.)

**SILICATE OF SODA.** The compounds of silica and soda are in all respects analogous to the preceding, but as carbonate of soda is not deliquescent, some of the soluble vitreous compounds which it forms effloresce on exposure, instead of running into a liquid, or remaining moist upon the surface. A solution of silica in soda has lately been employed as an addition to soap; it is said to improve its detergent powers.

**SILICATE OF LIME.** Silica and lime may be combined by fusion, but the results of their mutual action have not been minutely examined. Under the article **GLASS**, in Aikin's *Dictionary*, some valuable facts will be found in reference to these combinations. There are some minerals, and among them *table-spar* (composed of 50 silica, 45 lime), which are silicates of lime\*.

**SILICATE OF BARYTA.** Two parts of silica and one of baryta fuse together into a porous slag. A similar combination may be obtained with *strontia*.

**SILICATE OF MAGNESIA.** Several minerals appear to be definite compounds of silica and magnesia. *Olivin*, or *chrysolite*, is a simple silicate of magnesia ( $M + Si'$ ) with variable proportions of oxide of iron. *Steatite* is a tersilicate of magnesia ( $M + 3 Si'$ ), and *meerschbaum* a hydrated bisilicate. According to Morveau, silica and magnesia may be combined by fusion at a white-heat.

**SILICATE OF LIME OF MAGNESIA.** *Pyroxene*, or *augite*, is a crystallized mineral composed of 1 atom of bisilicate of lime, and 1 of bisilicate of magnesia. Sometimes oxide of iron replaces part of the magnesia. Similar crystals are occasionally found in the slags of iron-furnaces, and may also be formed artificially. (Mitscherlich and Berthier, *Ann. de Chim. et Phys.*, xxiv., 355.) Equal parts of lime, magnesia, and silica, may be fused into a green glass, which strikes fire with steel. (Achard.) *Amphibol*, or *Hornblende*, may be regarded as a compound of 1 atom of tersilicate of lime, and 3 of bisilicate of magnesia (with oxides of iron and manganese).

**SILICATE OF MANGANESE.** This compound occurs native in Dalecarlia. The red siliceous manganese is a bisilicate of the protoxide of manganese. ( $MAN + 2 Si'$ .)

**SILICATE OF IRON.** A silicate and bisilicate of protoxide of iron is found in the slag from the smelting of the ferro-sulphurets of copper. Davy found the ochraceous sediment of the chalybeate springs of Lucca to consist of *silicate of peroxide of iron*, the water probably holding a protosilicate in solution. There are several other minerals which are silicates, or hydrated silicates of iron.

**SILICATE OF ZINC** occurs native under the name of *electric calamine*: it crystallizes in rhombic prisms, composed of 2 atoms of silicate of oxide of zinc, and 1 of water.

**SILICATE OF COPPER** is thrown down upon the mixture of sulphate or nitrate of copper with silicate of potassa. It occurs native in *diopase*, or *copper-emerald*, which is apparently composed of 2 atoms of oxide of copper, 3 of silica, and 2 of water.

**SILICATE OF LEAD.** This compound exists in flint-glass, and is often used as a glaze for porcelain or earthenware, hence the poisonous quality conferred upon certain articles of food, when kept in earthen vessels thus glazed. A silicate of lead is easily formed (of variable composition) by fusing silica with oxide of lead; a yellow glass is the result. Some of the Chinese figures (often said to be made of rice) are a glass composed of 41 oxide of lead, 39 silica, 7 alumina. (Klaproth.)

Apophyllite is a *hydrated silicate of* lime, and 16 water. [ $(P + 3 si') + 8 (C$   
*lime and potassa*, composed of 1 atom of |  $+ 3 si') + 16 q.$ ]  
 tersilicate of potassa, 8 of tersilicate of

**SILICATE OF ALUMINA.** The different kinds of *clay* are probably mixtures, rather than compounds, of silica, alumina, and water\*. The mineral called *Cyanite* (Disthene), which is not uncommon in primitive rocks, is a *disilicate of alumina* ( $2\text{Al} + \text{Si}'$ ). *Andalusite* is also a silicate of alumina.

There are many ternary and quaternary silicates in the mineral kingdom, a few of which I shall here enumerate, selected chiefly from the account of them given by L. Gmelin†. *Topaz* = 2 silicate of alumina + 1 fluoride of aluminum. *Felspar* = 1 tersilicate of potassa + 3 tersilicate of alumina. *Leucite* = 1 bisilicate of potassa + 3 bisilicate of alumina. *Mica*, a silicate of alumina with tersilicate of potassa. *Pinit* = 1 tersilicate of potassa + 6 silicate of alumina (and oxide of iron). *Albite* = 1 tersilicate of soda + 3 tersilicate of alumina. *Sodalite* = 1 chloride of sodium + 2 silicate of soda + 6 silicate of alumina. *Nephelin* = 1 silicate of potassa + 2 silicate of soda + 12 silicate of alumina. *Analcime* = 1 bisilicate of soda + 3 bisilicate of alumina + 2 water. *Natrolite* = 1 tersilicate of soda + 3 silicate of alumina + 2 water. *Petalite* = 1 tersilicate of lithia + 3 tersilicate of alumina. *Spodumene* = 1 bisilicate of lithia + 4 bisilicate of alumina. *Barytic Harmotome* = 1 quatersilicate of baryta + 4 bisilicate of alumina + 6 water. *Axinite* = 1 bisilicate of lime + 3 silicate of alumina (with oxide of iron, manganese, and boracic acid?) *Prehnite* = 1 silicate of lime + 3 silicate of alumina. *Stilbite* = 1 tersilicate of lime + 3 tersilicate of alumina + 6 water. *Chabasite* = 1 bisilicate of lime + 3 bisilicate of alumina + 6 water. *Laumonite* = 1 bisilicate of lime + 3 bisilicate of alumina + 4 water. *Emerald* = 1 tersilicate of glucina + 2 tersilicate of alumina. *Euclase* = 1 silicate of glucina + 2 silicate of alumina. *Zircon* = silicate of zirconia, or 1 silica + 1 zirconia. *Sphene* = 1 tersilicate of lime + 1 sesquitanate of lime.

**POTTERY AND PORCELAIN.** The better kind of *pottery*, called in this country *Staffordshire ware*, is made of an artificial mixture of alumina and silica; the former obtained in the form of a fine clay, from Devonshire chiefly; and the latter, consisting of chert or flint, which is heated red-hot, quenched in water, and then reduced to powder. Each material, carefully powdered and sifted, is diffused through water, mixed by measure, and brought to a due consistency by evaporation: it is then highly plastic, and formed upon the potter's wheel and lathe into various

\* The best clays for the purposes of pottery consist of about 3 proportionals of silica and 1 of alumina; or by weight 48 and 18. The following are the principal varieties used here. 1. *Porcelain Clay*, derived principally from the decomposition of felspar, and containing silica and alumina, sometimes with traces of oxide of iron; it is very difficult of fusion. 2. *Marly Clay*, which, with silica and alumina, contains a portion of carbonate of lime; it is much used in making pale bricks, and as a manure; and when highly heated enters into fusion. 3. *Pipe Clay*, which is very plastic and tenacious, and requires a higher temperature than the preceding for fusion; when burned it is of a cream-colour, and used for tobacco-pipes and white pottery. 4. *Potters' Clay*, is of a reddish or gray colour, and becomes red when heated; it fuses at a bright red-heat: mixed with sand it is manufactured into red bricks and tiles, and is also used for coarse pottery.

† The numbers imply atoms or equivalents, according with those above given. It is obvious that very different views of the atomic constitution of minerals may be taken, from those given in the text: and as yet we have no experiments to guide us in our decisions on this point.

circular vessels, or moulded into other forms, which, after having been dried in a warm room, are enclosed in baked clay cases resembling band-boxes, and called *seggars*; these are ranged in the kiln so as nearly to fill it, leaving only space enough for the fuel; here the ware is kept red-hot for a considerable time, and thus brought to the state of *biscuit*. This is afterwards *glazed*, which is done “by dipping the biscuit-ware into a tub containing a mixture of about 60 parts of litharge, 10 of clay, and 20 of ground flint, diffused in water to a creamy consistence, and when taken out, enough adheres to the piece to give an uniform glazing when again heated. The pieces are then again packed up in the *seggars*, with small bits of pottery interposed between each, and fired in a kiln as before. The glazing-mixture fuses at a very moderate heat, and gives an uniform glossy coating, which finishes the process when it is intended for common white ware.” (Aikin’s *Dictionary*. Art. POTTERY.)

The patterns upon ordinary porcelain, which are chiefly in blue, in consequence of the facility of applying cobalt, are generally first printed off upon paper, which is applied to the plate or other article while in the state of biscuit; the colour adheres permanently to the surface when heat is properly applied.

The manufacture of *porcelain* is a most refined branch of art; the materials are selected with the greatest caution, it being necessary that the compound should remain perfectly white after exposure to heat: it is also required that it should endure a very high temperature without fusing, and at the same time acquire a semivitreous texture and a peculiar degree of translucency and toughness. These qualities are united in some of the oriental porcelain, or *China*, and in some of the old Dresden, but they are rarely found co-existent in that of modern European manufacture. Some of the French and English porcelain, especially that made at Sèvres and at Worcester, is extremely white, and duly translucent, but it is more apt to crack by sudden changes of temperature; more brittle, and consequently requires to be formed into thicker and heavier vessels; and more fusible than the finest porcelains of Japan and China.

The colours employed in painting porcelain are the same metallic oxides used for colouring glass, and in all the more delicate patterns they are laid on with a camel-hair pencil, and generally previously mixed with a little oil of turpentine. Where several colours are used, they often require various temperatures for their perfection; in which case those that bear the highest heat are first applied, and subsequently those which are brought out at lower temperatures. This art of painting on porcelain or in enamel is of the most delicate description; much experience and skill are required in it, and with every care there are frequent failures; hence it is attended with considerable expense. The gilding of porcelain is generally performed by applying finely-divided gold mixed up with gum-water and borax; upon the application of heat the gum burns off, and the borax vitrifying upon the surface causes the gold firmly to adhere; it is afterwards burnished.

CRUCIBLES. In the manufacture of various kinds of pottery employed in the chemical laboratory, and especially in regard to *crucibles*, many difficulties occur; and many requisites are necessary, which cannot be united in the same vessel: to the late Mr. Wedgwood we are indebted

for vast improvements in this as well as in other branches of the art. Crucibles composed of one part of pure clay mixed with about three parts of coarse and pure sand, slowly dried and annealed, resist a very high temperature without fusion, and generally retain metallic substances; but where the metals are suffered to oxidize, there are few which do not act upon any earthen vessel, and some cause its rapid fusion, as the oxides of lead, bismuth, &c. Where saline fluxes are used, the best crucibles will always suffer, but platinum may often be employed in these cases, and the chemist is thus enabled to combat many difficulties which were nearly insurmountable before this metal was thus applied. Whenever siliceous and aluminous earths are blended, as in the mixture of clay and sand, the compound softens, and the vessel loses its shape when exposed to a long-continued white heat, and this is the case with the *Hessian* crucibles: consequently, the most refractory of all vessels are those made entirely of clay, coarsely-powdered burned clay being used as a substitute for the sand. Such a compound resists the action of saline fluxes longer than any other, and is therefore used for the pots in glass-furnaces. A *Hessian* crucible lined with purer clay is rendered much more retentive; and a thin china cup, or other dense porcelain, resists the action of saline matters in fusion for a considerable time. Plumbago is a very good material for crucibles, and applicable to many purposes: when mixed with clay it forms a very difficultly fusible compound, and is protected from the action of the air at high temperatures; it is well calculated for small table-furnaces. Wrought-iron, and the best cast-iron crucibles, are used for the fusion of several metallic substances which melt at a bright red-heat. The latter are used in the Mint for the fusion of silver; the gold is melted in black-lead or plumbago-pots.

**LUTES.** Under the term *Lutes* a variety of compounds are used by the practical chemist for the purpose of securing the junctures of vessels or protecting them from the action of heat. Slips of wetted bladder, linseed meal made into a paste with gum-water, white of egg and quicklime, glaziers' putty, which consists of chalk and linseed oil, and *fat lute*, composed of pipe-clay and drying oil, well beaten to a stiff mass, are very useful lutes for retaining fumes and vapours and joining vessels to each other, but earthy compounds are required to withstand the action of a high temperature. Windsor loam, or an artificial mixture of clay and sand well beaten into a stiff paste, and then thinned with water and applied by a brush in successive layers, to retorts, tubes, gun-barrels, &c., enables them to bear a very high temperature; if a thick coating is required, great care should be taken that the cracks are filled up as it dries, and often a little tow mixed up with the lute renders it more permanent and applicable. If the lute is intended to vitrify, as for instance, to prevent the porosity of earthenware at high temperatures, a portion of borax or of red-lead may be mixed up with it. Respecting the selection and management of crucibles, lutes, &c., the reader is referred to Mr. Faraday's *Manipulation*.

**MORTARS AND CEMENTS.** *Mortar*, or the cement used in building, is a compound of several earthy substances, one of which is always lime; for much valuable information relating to this important subject we are indebted to the late Mr. Smeaton, (*History of the Eddystone Lighthouse*),

and an excellent summary of the principal facts connected with it will be found in Aikin's *Dictionary*. (Art. CEMENTS.) The ordinary mode of making mortar consists in mixing a quantity of common sand with slaked lime, without any careful attention to the quantity or purity of the materials; but it has been shown by Mr. Smeaton, that the presence of unburnt clay prevents the induration of the mortar, and the sand used in London always contains it; the lime too is often imperfectly burned and seldom duly selected; that which contains a portion of alumina and oxide of iron being preferable to the purer varieties: hence the advantage of *Dorking* lime, or *meagre lime*, as it is usually called. The sand should be sharp and large grained, and perfectly free from salt, which always prevents the mixture from becoming hard. The addition of calcined ferruginous clay, or calcined basalt, or black oxide of iron, gives mortar the property of becoming hard under water.

The mutual action which the substances constituting the different kinds of mortar undergo, has hitherto been but imperfectly examined by the chemist; to M. Vicat we are indebted for a curious and important series of investigations upon this subject, and his work may be consulted with much advantage, by those who are concerned in investigations of this nature. (*Recherches Expérimentales sur les Chaux de Construction, les Bétons, et les Mortiers ordinaires*. Paris, 1818.)

MANUFACTURE OF GLASS. Of this important and extensive subject I have only room for a very brief outline: for details I must refer to the authorities quoted, and to the volume of Dr. Lardner's *Cyclopædia*, which treats upon the manufacture of glass and pottery.

GLASS is essentially a compound of silica with potassa or soda, a variety of other substances being occasionally added for particular purposes, among which oxide of lead is perhaps the most important. The silica used in the manufacture of glass is of various degrees of purity; fine white sand is generally employed in this country; flints, and the white quartz pebbles, abundant in some rivers, are also occasionally used. The alkali is either potassa or soda; purified soda or pearlash being preferred for fine glass; while less pure alkalis, such as wood-ash, barilla, and kelp, are used for common glass, where the impurities contained in those substances are of no importance. The alkali is always used in the state of carbonate, but it loses its carbonic acid during combination with the silica; the quantity employed is about half the weight of the silica, but there is some loss during the process, by evaporation\*.

\* All common glass when reduced to a fine powder is more or less acted on by boiling water, which separates the alkali, and its entire disintegration seems only to be prevented by the insolubility of the silica. Indeed, if finely-powdered flint-glass be placed upon turmeric-paper and merely moistened, it powerfully reddens the test. Glass which has long been exposed to the weather frequently exhibits a beautiful iridescent appearance, and is so far decayed that it may be scratched with the nail: several years ago I examined some bottles of wine

which had lain in a wet cellar near the Bank, upwards of 150 years, having been deposited there (as circumstances proved) previous to the great fire of London in 1666. The glass was soft and greatly corroded upon the surface, in consequence of the abstraction of its alkali. The wine appeared to have been Malaga and Claret: the latter had perished, but the former was still vinous. See *Quarterly Journal*, xx. 262, where there is a paper on the solubility of glass, by Mr. T. Griffiths.

A glass composed solely of silica and alkali requires a very high temperature for its perfect fusion, and is very difficult to work, so that various substances are added, with the intention of forming a more fusible, colourless, dense, and transparent compound: *oxide of lead*, in the form of litharge or minium, is very efficacious in this respect; it increases the fusibility of the compound, gives it greater tenaciousness when red-hot, increases its refractive power, and enables it to bear sudden changes of temperature. It is a copious ingredient in the *London flint-glass*, celebrated for its brilliancy when cut, and used for most optical purposes. But lead, though it confers these advantages, is productive of some evil; it renders the glass so soft as easily to scratch, and so fusible that it softens at a dull red-heat, a quality which, though sometimes desirable, is often disadvantageous in its chemical applications. It is also very difficult to obtain a mass of glass containing lead, of equal density throughout; it is generally wavy, a defect especially felt in selecting glass for optical purposes.

Boracic acid and borax form an admirable flux for glass-making, but the expense of those materials confines them almost entirely to the manufacture of artificial gems, or of glass applicable to particular purposes only.

Black oxide of manganese has long been used in glass-making; it was formerly called *glass-soap*, a term implying its power of cleansing certain impurities, and especially the green tinge which is apt to arise from impure alkali; but if it be added at all in excess, it communicates a purple tinge, more or less intense according to its quantity. This purple hue is destroyed by charcoal, or by thrusting a billet of wood into the glass-pot, which causes a slight effervescence, and the colour disappears. There can be little doubt that the carbon acts by deoxidizing the manganese, for if a little nitre be added, the purple colour returns. Lime in very small quantities (8 or 10 parts of chalk to 100 of silica) is sometimes added to glass: it acts as a flux, but it endangers the transparency of the compound.

White arsenic is also used as a very cheap and powerful flux; and nitre, in small quantities, is employed to destroy any impurities arising from carbonaceous matter.

The materials for the manufacture of glass are sometimes submitted to an operation called *fritting*, before they are transferred to the regular glass-furnace. It consists in exposing them to a dull red-heat, by which moisture and carbonic acid are expelled, and a slight degree of chemical action induced; this also prevents the excessive swelling up of the materials in the glass-pots, and renders the process of vitrification more certain and expeditious. The term *frit*, however, is now generally applied to the mere mixture of materials, which, without previous preparation, are at once melted in the furnace.

The glass-pots are placed round a dome-shaped furnace, built upon arches, and open beneath for the free admission of air; there are generally six in each furnace, and they are entirely enclosed except at an orifice on the side, opening into a small recess formed by the alternate projections of the masonry and the flues, in which recess the workmen stand. Coal is the fuel employed, and the furnace is so built that a rapid current of

flame may be directed round each glass-pot, which afterwards passes out with the smoke into the dome and chimney, heating a broad covered shelf in its passage, which is sometimes used as an annealing-oven.

In the construction of the furnace and pots, the greatest care is required; especially in the latter, which have not only to resist long-continued heat, but also, as far as possible, the action of ingredients which tend to accelerate their fusion or vitrification. They are usually made entirely of a refractory clay, one portion being crude or unburnt, and another calcined and powdered; the latter being the remains of former furnaces when pulled down for repairs.

The frit is introduced into the glass-pots through the side-opening above mentioned, and being heated to bright redness, becomes of a pasty consistency, and at length perfectly fuses. A quantity of impurities subside to the bottom of the pot, and partly rise to its surface. The scum, known under the name of *sandever*\*, consists chiefly of saline substances, partly volatile at the high temperature of the furnace, which are removed from time to time, and sold to metal-refiners as a powerful flux. The sandever, or *glass-gall*, being separated, the materials gradually become clearer, abundance of air-bubbles are extricated, and at length the glass appears uniform and complete; the fire round the individual pot is then damped till its contents acquire a consistency fit for working, the whole process requiring about 48 hours from the time the pots are filled. At the working-heat, which is a full red, the glass has a very peculiar tenacious consistency, and as it adheres but feebly to polished metal, it is easily wrought and managed with iron tools.

All glass articles require to be carefully *annealed*, that is, suffered to cool very slowly, otherwise they are remarkably brittle and apt to crack, and even fly into many pieces upon the slightest touch of any hard substance, as is well shown in the small drops of green glass suddenly cooled by dropping them into water, and called *Rupert's drops*; the instant their thin end is broken off, they crumble into a powder with a kind of explosion. This phenomenon, according to Mr. Aikin, "depends upon some permanent and strong inequality of pressure, for when they are heated so red as to be soft, and merely let cool of themselves, the property of bursting is lost, and the specific gravity of the drop increased." What are termed *Proofs*, or *Bologna phials*, are also made of unannealed glass, and fly to pieces when a piece of flint or other hard and angular substance is dropped into them.

When large masses of glass which have been long in fusion are suffered to cool slowly, they frequently exhibit very singular crystalline appearances; there are often detached globular formations, of a very peculiar radiated texture, and looking exactly like foreign substances imbedded in the glass; sometimes it is opaque and crystalline, bearing a strong resemblance to certain mineral products: in these cases, crystallization seems to have influenced the affinity of the elements, and the consequent composition of the products. Mr. Watt's experiments upon the fusion of basalt may be consulted in reference to this curious subject. (*Phil. Trans.*)

\* This substance is scarcely known in our present glass-houses, in consequence of the pains bestowed upon the purification of the materials employed.



The exact composition of the different kinds of glass is scarcely known\*; the following proportions of the materials are, however, given in Messrs. Aikin's *Dictionary*, to which the reader is referred for a valuable article upon the subject of glass: it must, however, be recollected, that the composition of the perfect glass can only be remotely anticipated from a knowledge of the substances employed in its formation, in consequence of the changes which they undergo, and the volatility of some of them, at the high temperature to which they are subjected.

*Flint-glass.* Specific gravity about 3.2.

120 parts of fine clear white sand  
 40 „ purified pearlash  
 35 „ litharge  
 13 „ nitre  
 A small quantity of black oxide of manganese.

*Crown-glass*, or best window-glass.

200 parts of soda  
 300 „ fine sand  
 33 „ lime  
 250 „ ground fragments of glass †.

*Green Bottle-glass.*

100 parts of sand  
 30 „ coarse kelp  
 160 „ lixivated earth of wood-ashes.  
 30 „ fresh wood-ash  
 80 „ brick clay  
 100 „ fragments of glass.

*Plate-glass*, invented by Abraham Thevart in 1688, was first manufactured in Paris. It may be composed of

300 lbs. fine sand  
 200 lbs. soda  
 30 lbs. lime  
 32 oz. manganese  
 3 oz. cobalt azure  
 300 lbs. fragments of good glass.

These materials are brought into perfect fusion, and poured upon a hot iron or copper-plate; the mass is then rolled out, annealed, and afterwards polished by grinding with sand, emery, and colcothar. The difficulty of producing a perfect plate without specks, bubbles, or waves, may easily be conceived, and this, with the risk of breakage, renders a large plate extremely expensive.

\* Mr. Faraday has communicated to the Royal Society a paper on the manufacture of glass for optical purposes, containing much curious and valuable information upon the subject generally, and which should be consulted by those who are concerned in that difficult branch of the art of glass-making. He successfully availed himself of the use of *borate of lead* as one of its components. I am indebted to him for the following analyses of different specimens of flint glass.

Silica . . . . .	51.93	48.24	44.30
Oxide of lead . . . . .	33.28	40.12	43.05
Potassa . . . . .	13.77	10.60	11.75
Alumina . . . . .	0.47	0.58	0.50
Oxides of iron and manganese } . . . . .	0.27	0.08	0.12
	<hr/>	<hr/>	<hr/>
	99.72	99.62	99.72

† In the manufacture of all common glass a proportion of broken glass is usually mixed up with the raw materials, and is technically known under the name of *Cullet*.

The art of *colouring glass*, and of making *artificial gems*, is of an old date, and effected by metallic oxides. The *paste* for artificial gems generally contains borax, and should be kept in fusion till perfectly clear. The following proportions are recommended by M. Douault-Wieland. (*Ann. de Chim. et Phys.*, xix., 57.)

	Grains.
Powdered rock-crystal . . . . .	4056
Red lead . . . . .	6300
Pure potassa . . . . .	2154
Borax . . . . .	276
White arsenic . . . . .	12

M. Lançon gives the following as ingredients for a good paste:

	Grains.
Litharge . . . . .	100
White sand . . . . .	75
White tartar or pot-ash . . . . .	10

The metals employed as colouring-materials are: 1. Gold. The purple of Cassius imparts a fine ruby tint. 2. Silver. Oxide or phosphate of silver gives a yellow colour. 3. Iron. The oxides of iron produce blue, green, yellow, and brown, depending upon the state of oxidizement and quantity. 4. Copper. The oxides of copper give a rich green; they also produce a red when mixed with a small proportion of tartar, which tends partially to reduce the oxide. 5. Antimony imparts a rich yellow. 6. Manganese. The black oxide of this metal, in large quantities, forms a black glass; in smaller quantities, various shades of purple. 7. Cobalt, in the state of oxide, gives beautiful blues of various shades; and with the yellow of antimony or lead it produces green. 8. Chrome produces fine greens and reds, depending upon its state of oxidizement.

The following are the best authorities upon the subject of coloured glasses and artificial gems: Neri, *Art de la Verrerie*. Kunckel. Fontanieu, *Encyclopédie Méthodique*. *Ann. de Chim. et Phys.*, xiv., 57. Aikin's *Dictionary*, art. GLASS. Lardner's *Cyclopædia*.

*White Enamel* is merely glass, rendered more or less milky or opaque by the addition of oxide of tin; it forms the basis of many of the coloured enamels, which are tinged with the metallic oxides. Directions for the preparation of several good *enamel-colours* are given by Mr. Wynn, in the *Transactions of the Society of Arts*, 1817, and *Phil. Mag.*, li.

[It was my intention to have concluded this chapter with some general remarks upon the *chemical composition of rocks and soils*, and to have added a section on *geological chemistry*: but the extent of the subject, on examining my notes in reference to it, is such, that to do it justice, would require space that could not be spared in this already bulky volume, without abridging the contents of the ensuing chapters "on the Chemistry of the Products of Organization;" a branch of the science which has lately assumed so important an aspect, as to induce me to bestow upon it a larger share of the volume than was originally contemplated.]

















